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LOCAL BACKGROUND CONCENTRATION OF HEAVY METALS IN VARIOUS SOIL TYPES FORMED FROM GLACIAL TILL OF THE INOWROCŁAWSKA PLAIN

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Abstract

In the present study, local background concentrations of heavy metals were determined in soils which have been minimally influenced by human activities. The ground moraine landscape of the Inowrocławska Plain is dominated by Phaeozems, which occur in numerous associations with Luvisols and Cambisols. Four profiles of Phaeozems, three profiles of Luvisols and two profiles of Cambisols had been researched earlier, especially their morphology, selected physicochemical properties, texture and mineralogical composition. Selected properties were also measured to determine their influence on the content and distribution of trace elements in soil profiles. For determination of the concentration of metals in the soil profiles, the following indices were used: distribution factor (DI), enrichment factor (EF) and transfer factor (TF). The total content of metals in the genetic horizons and the local geochemical background level of metals in soils were determined. With the knowledge of the natural content of elements in the parent material, assumed to be the geochemical background, a degree of contamination of surface soil horizons can be evaluated. The content of Zn, Cu, Ni, Pb, Cr, Mn (mg kg^{-1}) and Fe and Ti (g kg^{-1}), which was defined as the content of the local background, was: 40.6; 12.6; 14.3; 12.9; 5.5; 309.9 and 16.5; 1.4, respectively. The distribution of Ni, Cr, Cu, Mn and Fe in the soil profiles can be explained as the effect of pedogenic factors, although in the case of, a tendency towards accumulation of Zn and Pb in the humus horizons as a result of anthropogenic input was observed. The distribution of pedogenic Ni, Cu, Cr and Mn was influenced by specific adsorption of metals on Fe oxides. The results indicate that the metals were bound more strongly to iron oxides than to organic matter. Based on the results of geochemical studies on selected arable soils from the Iowrocławska Plain, an integrated method was applied to assess the local background using an iterative 2s-technique (mean + 2 standard deviation). The relationships between trace elements and the conservative element such as Fe were

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used to predict the expected values of trace elements in topsoil. The results substantiate the importance of determining local background concentrations.

Key words: geochemical background, trace elements, arable soils.

LOKALNA ZAWARTOŚĆ TŁA GEOCHEMICZNEGO METALI CIĘŻKICH W RÓŻNYCH TYPACH GLEB WYTWORZONYCH Z GLINY ZWAŁOWEJ RÓWNINY INOWROCŁAWSKIEJ

Abstrakt

W badaniach określono zawartości tła geochemicznego metali ciężkich w glebach, które były przekształcone przez człowieka w niewielkim stopniu. W krajobrazie moreny dennej Równiny Inowrocławskiej dominują czarne ziemie będące w licznych asocjacjach glebowych z glebami płowymi i brunatnymi. Cztery profile czarnych ziem, trzy profile gleb płowych i dwa profile gleb brunatnych były przedmiotem wcześniejszych badań, które dotyczyły ich budowy morfologicznej, wybranych właściwości fizykochemicznych, uziarnienia oraz składu mineralogicznego. Oznaczono wybrane właściwości gleb mające wpływ na zawartość metali oraz ich dystrybucję w profilu glebowym. Określając koncentrację metali w profilach gleb, wykorzystano następujące wskaźniki: wskaźnik dystrybucji (DI), wskaźnik wzbogacenia (EF) oraz wskaźnik przemieszczenia (TF). Oznaczono całkowitą zawartość metali w poziomach genetycznych oraz określono zawartości lokalnego tła geochemicznego. Naturalne zawartości metali w skale macierzystej, uznane jako tło geochemiczne, są niezbędne do oceny stopnia zanieczyszczenia poziomów powierzchniowych gleby. Zawartości lokalnego tła geochemicznego dla Zn, Cu, Ni, Pb, Cr, Mn (mg kg^{-1}) oraz Fe i Ti (g kg^{-1}) wynoszą odpowiednio: 40,6; 12,6; 14,3; 12,9; 5,5; 309,9 oraz 16,5; 1,4. Rozmieszczenie Ni, Cr, Cu, Mn i Fe w profilach badanych gleb należy tłumaczyć wpływem czynników pedogenicznych, natomiast w przypadku Pb i Zn zaobserwowano tendencję ich akumulacji w poziomach próchnicznych w wyniku antropogenezy. Rozmieszczenie Ni, Cu Cr oraz Mn było spowodowane specyficzną adsorpcją na tlenkach żelaza. Wyniki badań wskazują, że więcej metali było związanych z tlenkami żelaza aniżeli z materią organiczną.

Opracowując wyniki badań gleb uprawnych Równiny Inowrocławskiej, zastosowano zintegrowaną metodę do oszacowania tła geochemicznego. W tym celu wykorzystano metodę iteratywną 2 s (średnia + 2 wartości odchylenia standardowego). Relacje między metalami a konserwatywnym elementem, jakim jest Fe, wykorzystano w celu oszacowania spodziewanych zawartości pierwiastków śladowych w poziomach wierzchnich gleb. Wyniki badań wskazują na potrzebę określenia lokalnego tła geochemicznego.

Słowa kluczowe: tło geochemiczne, pierwiastki śladowe, gleby uprawne.

INTRODUCTION

Origin of trace elements in soils

Trace elements enter into an agricultural ecosystem through natural and anthropogenic processes. The content of trace metals in soils depends on the mineralogical composition of the geologic parent material and on the weathering processes to which the soil forming materials have been subjected (ADRIANO 1986). The behaviour of trace metals in soils is related to their origin and chemical forms at the time of impaction (ALLAWAY 1990). Lithogenic metals are primarily inherited from the parent material. Pedogenic metals are of lithogenic and anthropogenic origins but their distribution in soil profiles changes due to mineral transformation and other pedogenic processes. Anthropogenic heavy metals are deposited into soils as a result of human activities (KABATA-PENDIAS 2004). Colloidal materials and clay minerals are generally surface-active and iron/manganese oxide surface coatings play an important role in the distribution of trace metals in soil profile. Metals fixed by Al, Fe and Mn hydrous oxides and other crystalline solid components are hardly mobile. The behaviour of pedogenic metals reflects several soil properties, of which pH and redox potential are the most important parameters. Anthropogenic metals are generally more mobile than lithogenic and pedogenic ones, whose origins are difficult to distinguish (KABATA-PENDIAS 1993). The duration and intensity of pedogenic processes, and parent material characteristics significantly determine the type and distribution of soil in landscape. Pedogenic processes clearly modify soil material by weathering and leaching minerals, adding organic matter, redistributing (clay illuviation) and transforming material (*in situ* clay formation). The pedological factors involved in distribution of trace elements in a soil profile include surface enrichment, leaching, translocation and mobilization (ALLOWAY 1990). The distribution of pedogenic trace metals is influenced by the specific adsorption of metals on various soil constituents. Generally, soil horizons rich in clay fraction or organic matter have higher contents of trace elements than sandy horizons. Metals accumulate in fine-particle size fraction in soils due to high surface areas and negative charges associated with clay minerals (e.g. smectite and vermiculite) and humic substances. Metal content in soil samples are commonly used to assess contamination, however, the accumulation of metals in soils increases with the decreasing particle size (ACOSTA et al. 2009). The main factors controlling the behaviour of trace metals in soils are organic matter content, iron and manganese hydroxides and redox potential. KABATA-PENDIAS (1993) referred to minerals from the topsoil being richer in Cu and Cr than the same minerals from the parent material while Ni – more concentrated in minerals from the parent material than from the surface horizon of soil, which may reflect a higher mobility of Cr and Cu under chemical weathering. Certain elements, e.g. Mn, tend to accumulate in surface horizons, while others, like Cr, are often higher in subsurface horizons. The content of trace metals in topsoil are likely to increase with growing industrial and agricultural activities. Due to many anthropogenic sources of pollution, it is important to estimate the geochemical background concentration of trace elements in soils. The geochemical background levels of trace metals should represent their natural concentration. The atmosphere plays a key role in global metal cycles as it receives inputs from many sources. Trace metals are transported and deposited having been released into the atmosphere due to natural processes and anthropogenic activity (PACYNA, PACYNA 2001). Assessment of concentrations of trace metals in the geological parent material, generally accepted as the geochemical background, is necessary for determining the pollution degree of topsoil. The origin of parent materials and their texture determines the amount of heavy metals in Polish soils (Table1).

Trace elements in farmlands

Concentration of trace elements in soils is associated with geochemical and biological cycles and generally is influenced by anthropogenic factors such as agricultural practices, industrial activities, and waste treatment (Kabata-Pendias 2004). Contamination of soils with trace elements is caused by atmospheric deposition or by direct disposal on the soil, which includes industrial waste disposal, impurities in fertilizers and manure, sewage sludge and pesticides containing heavy metals. Repeated use of fertilizers and sewage sludge containing trace amounts of metals may cause contamination of soils on a large scale (He et al. 2005). Trace elements enter agroecosystems through anthropogenic processes, including input of heavy metals from fertilizers, organic manures, irrigation and wet or dry deposits, which depend on the nature of and distance to point sources. On farmland, the presence of lithogenic trace metals in soils results from vertical (parent material weathering and pedogenesis) and also lateral redistribution processes, including tillage homogenisation and erosion. The long-term effect of metal-enriched substances application (fungicides, pesticides, and herbicides, phosphates containing of Cd and Pb, farm manures, biosolids) may cause contamination on a large scale (McBride, Spiers 2001). Fungicides and pesticides containing Cu and Zn are widely used to protect plants, especially in orchards. Phosphate fertilizers are among other sources of heavy metal input into agricultural systems. On farmland with a long history of crop production, the concentration of trace elements in the soil upper horizon can be higher than that found in the parent materials. In assessments of soil contamination, especially in risk assessment procedures, more parameters, such as total carbon content, cation exchange capacity and soil reaction, are often necessary.

Terms and definitions of background values of trace elements concentration

The influence of the geological substrate on trace element concentrations of soils can cause developed on specific substrates to demonstrate aberrant trace elements loads. Commonly, the terms *background* and *baseline* are often used as synonymous. *Environmental background* is considered to be descriptive of the natural tendency of an environmental material in the absence of human influences, while an ‘environmental baseline’ is a summary of existing conditions and can include influences of human activities such as land use. Baize and Sterckemann (2001) applicate the term ‘pedogeochemical background’ in relation to natural concentration of elements in

Table 1

Arithmetic mean and/or range of total content of metals

Soil materials	Zn	Cu	Pb	Cr	Ni	Mn	Fe	References
	(mg kg^{-1})						(g kg^{-1})	
Boulder loams (middle texture) in northern and central Poland	30-51 (41.0)	4.0-13.6 (10.0)	6-16 (10.7)	20.0-48 (37.0)	12.6-20.- 6 (13.7)	228-457 (344.0)	1.51-2.42 (2.03)	Czarnowska (1996)
Bed-rocks in northern and central Poland	5-59 (30.0)	0.4-23.5 (7.1)	0.5-21 (9.8)	2-64 (27.0)	0.5-28.5 (10.2)	15-1040 (289.0)	0.11-3.70 (1.29)	Czarnowska (1996)
Sedimentary rocks of glacial origin in Poland	(36.0)	(8.8)	(10.3)	(30.0)	(12.7)	(322.0)		Czarnowska, Gworek (1990)
Soils in Poland 0-20 cm layer	(32.5)	(6.6)	(13.70		(6.3)			Piotrowska Terelak (1997)
Soils in the Kujawy and Pomorze region 0-20 cm layer	(23.8)	(4.7)	(12.6)		(6.3)			Piotrowska Terelak (1997)
Soils developed from glacial tills in WNP horizon-B – samples <0.06 mm	(19.0)	(3.0)				(300.0)		Gałuszka (2007)

WNP – Wigierski National Park

soils. In contrast, another term ‘anthropogenic background’ used by Portier (2001) defined concentrations typically observed in an area affected by human activities but that are not associated with a specific contamination activity. The natural abundance of an element in a rock, sediments, soil with references to a particular area is the most common definition of the term ‘geochemical backgrund’. The concept of ‘geochemical background’ comes originally from exploration geochemistry and was introduced to differentiate between normal concentration of element and anomalies, which might be indicative of an ore existence. Traditionally, geochemical anomaly is an aberration from the geochemical patterns that are normal for a given area. The term ‘threshold’, which describes the limit of normal background variation, was introduced to determine the difference between background and anomaly. The geochemical anomalies have been identified by setting threshold values, which mark the upper and lower limits of normal variation for a particular element. Values within the threshold values are referred to as background values and those above or below as anomalies but usually expressed as a single value showing the limit between anomalous and background concentrations. This definition is used mainly in exploration, and is not appropriate for environmental purposes. In environmental geochemistry, there are also problems with the definition of natural background concentration of trace metals. In the ISO document (ISO 2005) the term ‘ambient background concentration’ (ABC) has been used with the same meaning as that of ‘usual background concentration’. Ambient background concentration (ABC) of a trace metals may vary depending on soil types and land uses but consists of both a natural pedo-geochemical fraction and an anthropogenic fraction (Zhao et al. 2007). Soil parent materials and pedogenic processes clearly determined ambient background concentration of trace metals in soils. Reiman and Garrett (2005) introduced the term ‘ambient background’ that defines the unmeasurable perturbed and no longer original natural background. Many slightly elevated horizons or levels in soils reflect ambient background and are no longer pristine natural since natural background no longer exists. The term ‘natural background’ is widely used to describe background levels reflecting natural processes unaffected by human activities. Both effects will modify the ‘natural background’ at the location where the material is deposited, independent of natural or anthropogenic origin (Reimann, Garrett 2005). Therefore, the term natural background could be used as long as natural processes can still be noticed. Gałuszka et al. (2007) described that the background values are different for remote areas, and are governed primarily by the geologic setting of the region and it may be assessed only on a local or regional scale. Blaser et al. (2000) suggest that element concentration measured in a deeper soil horizon could be taken as a ‘local background’ for the surface horizon that is more possibly affected by anthropogenic contamination. Greatly higher element values in upper soil horizons are usually interpreted as evidence of anthropogenic input. A specific TOP/BOT ratio as an index of relative enrichment or depletion of metals in the topsoil horizon may, to certain extent, make sense on farmland, whereas, even for arable soil, a high value in the TOP/BOT-ratio is no evidence of contamination since the TOP-horizon is not 1:1 comparable to the BOT-horizon. The surface horizons are relatively depleted of the colloidal fraction. Clay fraction and oxyhydroxides commonly demonstrate much higher metals concentration than the coarser soil size fraction. Reimann et al. (2005), demonstrated that only several elements showed a general enrichment in the TOP-layer. Researchers have suggested that contamination is not the most likely explanation for enrichment. Zinc and manganese are often correlated to the abundance of organic matter and for lead the explanation that the enrichment is due to atmospheric input may be suggested. It is very important that regulators recognize that 'background' depends on location and scale. It changes from region to region and with scale of the area investigated. In another method, trace metals are measured in deeper soil horizon as the local background for the upper horizons, usually after correction for the variation of a reference element such as Zr. The relationships between trace elements and semi-conservative elements such as Fe, Al and Mn were used to predict the expected values of trace elements in topsoils.

The term 'geochemical baseline' is often used interchangeably with the term geochemical background, particularly when is used in environmental contexts and is very important in environmental legislation, which prescribes limits for heavy metals uncontaminated area. Baseline studies allow investigators to assess chemical pattern changes in the environment resulting from anthropogenic activity. A 'geochemical baseline' represents a measure of a given soil samples in specific location and time (Lee, Helsel 2005) and refers to the prevailing variation in the concentration of an element in the surface environment. Thus baselines must always be verified in any assessment of sites for contamination. Therefore, a 'geochemical baseline' or background should be described by regional variability and it is a function of time. The baseline concentrations, usually express as an observed or 95% expected range, represent a measure of a given sample in a singular location and time (Matschullat et al. 1999). They vary in regions of different pollution, but in pristine areas, geochemical baseline concentrations are close to background values. The normalization procedure is a widely used method to obtain the regional geochemical baseline. The measured trace elements have to be fitted with the references element not influenced by human activities. The baseline can be estimated for every single point that confirms to the linear regression conditions. Iron and alluminum as a constituent of aluminosilicate mineral are widely used as the reference elements (Donoghue et al. 1997, Zhang et al. 2007). Titanium and Sc have also been used as reference elements due to their characteristics of geochemical stability in the environmental compartments. A 'geochemical baseline' provides the means to distinguish between the pedogenic and the anthropogenic origin of trace element in the environmental compartments (Zhang et al. 2007). The term ‘geochemical baseline’ has not yet been defined clearly and most commonly it referred to the natural abundance of an element in particular material such as rock, sediments, and soil respect to a particular land. However, this term was used mainly in exploration rather than environment as it generally refers to a single value. Many times natural variation of element concentration in different environmental sample materials is often so large that it is difficult to identify anthropogenic addition and contamination. These should be restricted to the local scale (Reimann, Garrett 2005). A statistically determined background value and associated range cannot be used alone to detect anthropogenic influences on the environment; geochemical mapping at an appropriate scale is essential. To define «background» or «normal abundance», a considerable number of samples have to be collected over a sufficiently large area to be able to differentiate between different possible natural and anthropogenic sources. Jarva et al. (2010) concluded that geochemical properties to a great extent determine the distribution of metals in soil. Regional variations in the fine-fraction content of different tills reflecting glaciation processes define element concentration. An anthropogenic impact on baseline levels can be detected particularly in industrialised areas. Reinman and Garrett (2005) claimed that geochemical mapping at an appropriate scale is indispensable to create a map showing areas of relatively homogenous geochemistry. A particular map of geochemically homogeneous areas with other relevant information can be used to deduct the natural and anthropogenic processes that determine the distribution of metals.

Modes of chemical normalization

Since the background value for particular element is theoretical, different methods of assessing it, i.e. geochemical, statistical, and integrated methods, may be applied. Direct (empirical) and indirect (statistical) methods are used for assessing background concentrations of elements in specific area. The direct (geochemical) method of assessing background concentration bears on studies of samples not influenced by anthropogenic activities or to relatively pristine areas (Horckmans et al. 2005). There are selected statistical methods used not only for assessing background concentration but also for the separation of geochemical anomalies from the geochemical background. In statistical methods: the regression analysis, probability plots, and fractal method have been applied (Matschullat 2000). Some selected tests (iterative 2s-technic and calculated distribution function; 4σ-outlier test; Lepeltier method), were used to quantify the background concentration of trace metals in soils. Most statistical tests are only helpful in eliminating the so-called outliers, and thus to reduce the original detaset to a clean data collective. From reduced dataset the essential descriptive statistical parameters can be calculated. The normal range of a sample is defined by the mean $\pm 2\sigma$, this means that ca. 95% of the samples come within the range. The upper values describe the threshold level (mean $+2\sigma$), which means that ca.

97% of the samples lie below this value. The iterative 2σ-technic is also an appropriate method of background assessment and it corresponds to widely used threshold calculation with the formula: upper limit of mean ±2σ range (Li et al. 2003). Mean and standard deviation (σ) are calculated for the original dataset. All values beyond the mean ±2σ interval are omitted. The mean ±2σ calculated from the resulting sub-collective is considered to reflect the geoegenic background (Matschullat 2000). The definition of the background as «the normal range of a sample» (mean ±2σ) requests the assumption of a long-normal distribution.The linear relationships between the content of individual metal of concern and a conservative element (e.g. Fe, Al) content were defined in the form of $y=ax+b$, where y is the value of the metal, x is the Fe, Al content in the samples. The data lying out of the 95% confidence band were eliminated, and then there was created a new linear equation with the updated dataset where all the data were within the 95% confidence band. The measured element concentration has to be fitted with conservative elements that are not influenced by anthropogenic activities. The measured e.g. Fe, Al or Zr contents are predicted value for each element at each samples location was computed. The predicted mean value as the critical value and mean ±2σ as the range of the geochemical baseline for each element, where s is the standard deviation of predicted dataset (Covelli, Fontolan 1997). The study allowed estimating the amount of anthropogenically-introduced metals into the arable soils.

Chemical normalization was performed by comparing the analysed samples, to the nearby non-contaminated samples of similar texture, chemical and mineralogical composition. Background concentration of non-contaminated samples can be established from parent material samples (C-horizon), below the level of anthropogenic influences, of the same region. The level of contamination of soil with heavy metal is expressed in terms of a distribution index (DI) calculated as follows:

$$\text{Distribution Index (DI)} = \frac{\text{metal content in the solum horizon}}{\text{metal content in parent material}} \qquad (1)$$

where: DI < 1 refers to low contamination, 1 ≥ DI ≥ 3 means moderate contamination, 3 ≥ DI ≤ 6 indicates considerable contamination and DI > 6 indicates very high contamination. Potential pollutant concentrations are to be compared with background averages in order to calculate the enrichment factor (EF). To identify anomalous metal concentration, geochemical normalization of the trace elements data to a conservative element, such as Fe, Al, was applied (Bourennane et al. 2010). In this study iron has also been used as a conservative tracer to differentiate natural from anthropogenic components.

Enrichment factor (EF) is defined as follows:

$$\mathrm{EF} = \frac{\left(\frac{M}{\mathrm{Fe}}\right) sample}{\left(\frac{M}{\mathrm{Fe}}\right) background} \qquad (2)$$

where: M stands for ‘metal’.

ZHANG and LIU (2002) proposed that EF values between 0.5 and 1.5 indicate the metal is entirely from crustal or natural processes, whereas values greater than 1.5 suggest the possible anthropogenic impact in soils. Transfer factor (TF) is defined as follow:

$$\mathrm{TF}_h = (X_h / X_p) / (Y_h / Y_p) \qquad (3)$$

where X_h stands for the concentration of the metal in bulk soil sample in genetic horizon, X_p is the concentration of the Ti in bulk soil sample in genetic horizon; Y_h is the concentration of metal in parent material, Y_p stands for the concentration of Ti in parent material (ACOSTA et al. 2011). Values >1.0 indicate the accumulation of metals in soil profile due to soil forming processes. However values of 1.0 and <1.0 show that enrichment in metals is not detectable and loss of metals is due to pedogenic processes.

MATERIAL AND METHODS

Geological background concentrations of trace elements were determined for arable soils in the Inowrocławska Plain mezoregion, which are developed on the poorly sorted glacial till. The nine representative pedons were selected for research (Table 2). Soils developed from the Baltic glacial till, similar in age, and the same origin, with different water regime. In addition, there is no natural geochenical anomaly. Detailed characteristics of soils and their morphology, selected properties were given in the previous papers (KOBIERSKI, DĄBKOWSKA-NASKRĘT 2003a,b, KOBIERSKI et al. 2009). According to WRB taxonomy (IUSS WRB 2007), the soils from the region represent Phaeozems (profiles I, II, III, IV), Luvisols (profiles V, VI, VII) and Cambisols (profiles VIII, IX). Sampling sites with relatively small impacts of human activity were selected, and soil profile samples were analysed for Zn, Cu, Pb, Cr, Ni, Fe and Ti content. Moreover, usual data for soil characterization of some properties (e.g. pH, hydrolytic acidity; CEC, texture, organic carbon, total carbonates) were used. The soil was sampled from a particular genetic horizon, air-dried and sieved through a 2 mm screen. The depth of the horizons varied according to the soil development. In the Inowrocławska Plain region the soil-forming processes have greatly affected the initial composition inherited from parent material. The mean depth of the parent material in Luvisols and Cambisols was deeper than in Phaeozems. The following physical and chemi-

Table 2

Pedons location in the Inowrocławska Plain

No	GPS positioning		
I	Szadłowice	52° 50' 35.2" N	18° 20' 14.9" E
II	Cieślin	52° 48' 08.9" N	18° 12' 09.2" E
III	Gnojno	52° 59' 38.2" N	18° 15' 59.6" E
IV	Dobre	52° 41' 10.8" N	18° 35' 04.6" E
V	Liszkowo	52° 53' 26.2" N	18° 13' 53.5" E
VI	Zduny	52° 49' 35.9" N	18° 33' 22.9" E
VII	Rucewko	52° 44' 14.2" N	18° 05' 37.2" E
VIII	Batkowo	52° 45' 58.7" N	18° 12' 13.1" E
IX	Pęchowo	52° 56' 12.5" N	18° 04' 19.9" E

cal properties of soil were determined by standard methods used in analytical work: granulometric composition by Cassegrande method, pH in 1 M KCl dm^{-3} – potentiometrically, organic carbon (TOC) using TOCN Primacs Skalar Analyser, cation exchange capacity (CEC) was calculated on the basis of hydrolytic acidity and exchangeable bases determined with BaCl$_2$. Total Zn and Cu content were defined after HF and HClO$_4$ mineralization of homogenised soil samples according to Crock and Severson (1987). The analyses of element concentrations were conducted using atomic absorption spectrometer (Philips PU 9100X). The descriptive statistical analysis such as standard deviation, standard error, regression analysis mean for metals were calculated using Statistica 6.0 computer package. The relationships between the elemental composition were determined using correlation and cluster analysis. The cluster was performed with the method of weighted average linkage between the groups. Person's correlation method for the cluster intervals and the elements showing a close correlation were identified. Reference soil (SO-4) from the Canadian Certified Reference Materials Project (Bowman et al. 1979) and reagent blanks; replications were used as the quality control samples during the analysis. The results showed no sign of contamination and revealed that the precision and bias of the analysis were generally below 7%. The recovery rates for the metals in the standard reference material ranged from 89 to 112%. The recovery of metals in the analysis was within <5.0%, as compared to the reference soil material.

Soil research results for the Inowrocławska Plain

The original stage of soil formation is the accumulation of the parent materials. The northern part of the Polish land mass was glaciated during the last Baltic glacial episode, and therefore the majority of parent materials in mesoregions are of glacial origin and relatively young. Glacial till deposits are poorly sorted and heterogeneous mixtures of gravel, sand, silt, and clay with varying texture and mineralogy. The nature, properties and mineralogical composition of the parent materials exert a strong subsequent control on the pathways of soil genesis. Different types of soils from the Inowrocławska plain were formed from glacial sediments and they may further undergo transformations (KOBIERSKI et al. 2009). Granulometric indices confirm the presence of typical glacial till. In the upper horizons of soil fine sandy loam was dominated, however, in the parent material there was observed homogenous sandy loam (KOBIERSKI, DĄBKOWSKA-NASKRĘT 2003a, KOBIERSKI 2010b). Phaeozems and Cambisols from this region were formed under at least two processes including lessivage processes. The downward leaching of soluble ions and translocation of clays in soil profiles is related to the average depth to which water penetrates the soil. The content of calcium carbonate in parent material is very essential to buffering as $CaCO_3$ is able to neutralize soil acidity. Clay minerals and organic matter contents are also important to buffering and cation exchangeable capacities. Illite dominated the clay mineralogy in the soil analysed, other clay minerals such as smectite, chlorite and interstratified minerals (illit-smectie, chlorite-smectite) were also identified by XRD (KOBIERSKI, DĄBKOWSKA-NASKRĘT 2003b, KOBIERSKI et al. 2009).

Soils formed as a result of the interaction of soil factors and specific soil-formation processes currently undergo strong anthropogenic effect. An intensive agricultural cultivation of Luvisols in the Inowrocław Plain resulted in irreversible changes in their morphology, seen by including the Et horizon to Ap horizon. The evaluation of iron forms distribution in soil profiles show that it can be concluded that the Cambisols researched show qualities of stratified Luvisols (KOBIERSKI 2010a). The Fed/clay ratio profile distribution indicates comigration of clay fraction and free iron oxides in Phaeozems and Luvisols. Neutral and alkaline reaction and a considerable content of organic matter do not facilitate metals mobilisation, unlike the soils in which the degree of oxidation of iron is low under the conditions of low redox potential. A low content of active iron in the parent material of the soils researched can be referred to a relatively high content of calcium carbonate, which constitutes a geochemical barrier, decreasing the mobility of that metal (KOBIERSKI 2010a). A study of morphology of Phaeozems provides a clearer picture of recent changes in mineral phase due to soil texture, which influences the water regime in soil. Luvisols and Cambisols do not show any gleyic process traits.

RESULTS AND DISSCUSION

Some properties of the investigated arable soils are included in Table 3. The soils were neutral or alkaline, with the pH in KCl ranging from 6.70 to 7.90. Soils differed in texture and organic matter content, mean values for clay particles and organic matter contents were found in the range 7-17% and 7.9-15.2 mg kg^{-1} in humus horizon, respectively. Illuvial horizons of all the soils analysed were enriched in clay fraction. The cation exchange capacity (CEC) ranged from 29.6 to 194.5 mmol(+) kg^{-1} of soil. The lowest amounts of exchangeable cations were found in horizons Et but the soils were sorption-saturated. The horizons rich in clay fraction contained higher content of cations.

The mobility of trace elements depends not only on the total concentration in the soil but also on soil properties, and environmental factors. Metals accumulate in soil in various forms: water soluble, exchangeable, carbonate associated and Fe-Mn oxides associated, organic matter associated and residual forms. Experimental datasets have been tested by statistical analysis in order to evaluate the possibility of differentiating the sampling sites to identify possible correlations existing among metals and to assess relationships between the chemical composition and the anthropogenic influences. Geochemical association of trace metals in the soil is mostly determined by the local geological features, pedogenesis and the characteristics of trace elements. Soil forming processes cause variation in the distribution of elements. The different mineral composition and differences in soil texture are factors determining metals concentrations. Cu, Ni, Cr, Mn and Fe partly leach from the minerals and precipitate as colloidal particles. We have observed an accumulation of metals at 42-95 cm in soil profiles. Clay fraction and organic carbon content is generally considered to be important factors in evaluating the trace element concentration in soils (LIVENS 1991, SPARK et al. 1997, TACK et al. 1997). In this study no clear positive relationships between trace elements and organic carbon content was apparent but a negative limited association of Ni and Fe with organic carbon content could be seen (Table 4). A fairly linear relation was observed between Fe and metals such as Cu, Ni, Cr, Mn (Table 5). The correlation between Fe and trace elements content may be a relevant factor when determining background concentration levels. Figure 1 is the result of the cluster analysis for the metals of the topsoil and two main groups were distinguished in the dendrogram.

Cluster 1 consisted of Ni, Fe, Cu, Cr, Mn and Zn and cluster 2 included Pb. One can observe four sub-clusters for cluster 1 (a) Ni, Fe; (b) Cu; (c) Cr, Mn; (d) Zn, which indicated that Ni, Cu, Cr and Zn were mainly associated with Fe-Mn oxides and were relatively immobile in geochemistry. This implied that the first geochemical association was mainly influenced by local geological features. The accumulation could reflect an illuvial horizon loca-

Table 3

Selected properties of analyzed soils

No	Horizon	Depth (cm)	pH KCl	Corg (g kg^{-1})	Hh	S	CEC	Clay fraction (%)
					[mmol(+) kg^{-1}]			
I	Ap	0-32	7.27	15.1	2.5	146.2	148.7	14
	A2	32-56	7.90	10.2	0.2	158.5	158.7	14
II	Ap	0-28	7.05	10.5	3.3	140.6	143.9	13
	A2	28-40	6.97	10.2	3.9	136.2	140.1	12
	AB	40-55	7.44	7.3	0.2	161.4	161.6	16
	Bt	55-75	7.36	2.9	1.9	159.2	161.1	20
III	Ap	0-28	7.23	15.2	2.4	182.7	185.1	13
	A2	28-49	7.26	14.8	3.2	191.3	194.5	14
IV	Ap	0-26	7.28	12.2	3.0	153.5	156.5	13
	A2	26-42	7.77	10.6	1.1	185.9	187.0	14
	Bt	42-60	7.67	2.6	2.5	168.0	170.5	21
V	Ap	0-25	7.21	9.3	2.7	108.3	111.0	12
	Et	25-45	6.96	1.7	5.3	38.9	44.2	7
	Bt	45-95	7.03	1.5	3.9	138.8	142.7	24
VI	Ap	0-32	7.15	7.9	2.4	70.3	72.7	7
	Et	32-50	6.96	1.3	8.0	21.6	29.6	5
	Bt	50-89	7.16	1.8	6.4	154.4	160.8	24
VII	Ap	0-29	7.07	8.9	4.0	135.2	139.2	13
	Bt1	29-49	6.98	4.2	3.0	126.0	129.0	19
	Bt2	49-78	7.04	2.8	2.4	131.0	133.4	22
VIII	Ap	0-28	7.89	9.3	7.6	120.8	128.4	17
	Bw(t)1	28-50	7.86	4.1	8.3	144.4	152.7	23
	Bw(t)2	50-70	7.18	2.7	4.0	132.1	136.1	22
IX	Ap	0-26	7.17	9.0	3.0	109.6	112.6	12
	Bw(t)1	26-50	6.72	3.5	8.3	124.2	132.5	21
	Bw(t)2	50-70	6.70	3.0	6.7	119.9	126.6	23

Hh – hydrolytic acidity, S – base saturation, CEC – cation exchange capacity Bw(t) weakly developed luvic features in cambic horizon

Table 4

Correlation coefficients significant at $p<0.05$

Parameters	Zn	Cu	Ni	Cr	Mn	Fe	Ti
Corg			-0.54			-0.54	-0.70
Clay		0.81	0.94	0.53	0.40	0.95	0.70
CEC	0.57	0.64		0.40			
Zn		0.48					
Cu			0.79			0.74	0.70
Ni				0.50	0.41	0.95	0.79
Pb					0.50		
Cr					0.58	0.60	
Mn						0.52	
Fe							0.78

Table 5

Linear relationship between metals and Fe from topsoil

Equation	SEE	r	p
Cu = 0.37 Fe + 5.97	1.87	0.74	<0.001
Ni = 0.93 Fe - 1.43	1.75	0.95	<0.001
Mn = 4.83 Fe + 226.72	44.77	0.52	<0.001
Cr = 0.17 Fe + 2.73	1.27	0.60	<0.002

SEE indicates the standard error of Y extimation

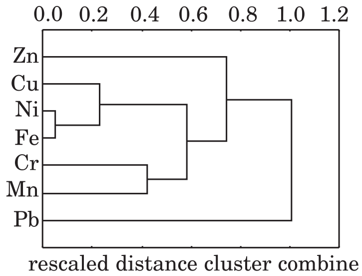

Fig. 1. Dendrogram using average linkage (between groups) to display the elements association in the soils

ted here in as much as trace elements are mostly associated with the clay fraction of soils. Therefore, it was attempted to use Fe as a proxy for clay fraction content in the clay-rich soil materials. A strong correlation was found between Fe and clay content for analysed profiles and so the comparison was properly used. Finally, the trace elements could also be translocated and then precipitated due to an increase in pH. In well-aerated acid soils several metals (especially Zn) are substantially more mobile and bioavailable than in poorly aerated neutral or alkaline soils (TACK, VERLOO 1995).

It is very important to determine the total metals content in arable soils in order to assess their quality and the potential risk of contamination. Determination of the total concentration should be complemented by the measurement of the labile fraction available to plants (KABATA-PENDIAS, PENDIAS 2001). Lead is generally considered to be a fairly immobile element, as well as a common pollutant, resulting from the long-range transport of aerial contaminants (PACYNA, PACYNA 2001). The limited mobility and strong complexation of Pb by organic matter result in the bioaccumulation of the element in humus surface horizons of soils. The highest amounts of metals found in the upper horizon (humus horizon) in comparison with subsurface horizons indicated a chelating role of organic matter in relation to metals (LIVENS 1991). Humic phenolic hydroxyl and carboxyl groups are mainly involved in the formation of metal-humic complexes (SPARK at al. 1997, COLES, YONG 2006).

The influence of the geological substrate on the content of trace metals is very important and can make soils developed on specific substrates demonstrate divergent trace elements loads. HORCKMANS et al. (2005) confirm the importance of using appropriate background levels for the assessment of contaminated soils and the necessity of determining background concentrations locally. Specific substrates with possibly unpredictable trace element loads can be present over extensive areas, designating it necessary to know the background concentrations before defining any conclusions as to whether elevated element concentrations in soil are lithogenic or anthropogenic. The geochemical baseline takes into account the geochemical variation in basic geology, the different geologic units and the influence of soil-forming processes but it also influences mineralization and anthropogenic effects (SALMINEN, GREGORAUSKIENE 2000).

A level of contamination of farmland in Poland was evaluated in two countrywide programs (TERELAK et al. 2000). The results of study indicated that 80% of agricultural land is characterised by natural and 17.6% – slightly elevated content of heavy metals. About 3% of arable soils are contaminated with heavy metals to various degrees. The expected range of metals content in farmland soils in Poland differs significantly from the state range, which clearly indicates that low as well as high metal concentrations in arable soil in Poland may appear infrequently (CZARNOWSKA, GWOREK 1990, CZARNOWSKA 1996, PIOTROWSKA, TERELAK 1997). The average Zn, Cu, Ni and Pb contents in farmland soils in Poland are 32.4, 6.5, 6.2, 13.6 mg kg^{-1} respectively (Oleszek et al. 2003).

The distribution index (DI) values ranged from 0.3 to 1.7, while enrichment factor (EF) values were higher and ranged from 0.6 to 2.5 (Tables 6, 7). In the Ap horizon most profiles and in a few cases in Et and Bt horizons there were found the highest values of both indices for respective metals. There was reported no anthropogenic effect on the content of nickel and an slight effect on the content of the other metals. Soil contamination assessment was carried out using enrichment factor and transfer factor (Figures 2, 3). The calculation of enrichment factors showed that Mn, Cu, Cr in humus horizon ranged from 0.8 to 2.0 and Ni, and Fe from 0.8 to 1.0, and Pb from 1.1 to 2.4 whereas Zn ranged from 0.9 to 2.4. Some of the elevated concentrations of Zn are probably due to anthropogenic sources, mainly fertilizers and pesticides used in agriculture. A long-term agricultural use of analysed soils resulted in a slight increase in the Pb, Zn, Cu content in the profiles of the soils, as compared with the contents determining the geochemical background. The pedogenic formation of Fe oxides seems to be a factor determining the distribution of trace metals in the depth of soil profile. The distribution of pedogenic Cu, Zn, Ni and Pb is influenced by the specific adsorption of metals on Fe oxides. There was found an effect of pedogenesis on the distribution of metals in the profiles of the soils, which refers to Ni and Fe since the transfer factor (TF) scored highest in subsurface horizons and the illuvial horizon of II, IV, V, VI, VIII, IX profiles (Figures 2, 3). The highest TF values for lead were reported in the Ap horizon in profiles V, VI, IX, which points to the effect of anthropogenic factors on the accumulation of that metal. The highest TF values in horizon Ap of soils I, II, III demonstrates a tendency to accumulate Zn, Cu and Pb as a result of a long-term agricultural use of soils of the Inowrocławska Plain. The distribution of metals in the soil profiles was most affected by the content of clay fraction, which was confirmed by the statistical analysis (Table 4). The distribution pattern of Zn and Cu in soil profiles of Phaeozems suggested an accumulation of these metals in the surface horizon but Cr and Ni are gradually leached down and accumulated in Bt horizon, which is conventional view for the mechanism of metals distribution in soil profiles. The clay fraction proved a strong mobility to fix the metals on their surface. The content of metals (arithmetic means) in the parent material of analyzed soils were considered to be the content of the geochemical background (Table 8). Respectively higher content for respective metals were found after the application of one of the statistical methods (mean + 2σ range).

The content of metals were similar to the ones presented by other authors describing the content of the geochemical background for respective metals in arable soils in analyzed region (Dąbkowska-Naskręt et al. 2000, 2006).

Table 6

Content of Zn, Cu, Ni, Pb (mg kg^{-1})

No	Horizon	$\frac{\text{AM}}{\text{s.e.}}$	Zn	DI	EF	Cu	DI	EF	Ni	DI	EF	Pb	DI	EF
1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
I	Ap		67.4	1.1	2.1	12.6	1.1	1.3	10.1	0.7	0.9	12.1	1.0	1.2
	A2		57.4	1.0	1.7	12.4	1.0	1.2	11.3	0.8	0.9	11.7	1.0	1.1
	Ckg	(n=3) s.e.	58.5 3.5			11.9 0.3			14.2 1.0			11.7 0.7		
II	Ap		72.7	1.7	2.4	10.8	0.9	1.1	9.1	0.7	0.8	13.1	0.9	1.3
	A2		52.2	1.2	1.7	10.1	0.9	1.0	9.7	0.7	0.8	12.6	0.9	1.2
	AB		55.3	1.3	1.4	10.7	0.9	0.9	13.1	0.9	0.9	14.7	1.0	1.1
	Bt		58.7	1.3	1.2	12.0	1.0	0.8	17.2	1.2	1.0	12.2	0.8	0.8
	Ckg	(n=3) s.e.	43.5 5.1			11.6 1.0			13.7 1.3			14.5 1.2		
III	Ap		45.4	1.2	1.6	14.2	1.2	1.6	10.8	0.8	1.0	13.0	1.0	1.4
	A2		44.2	1.1	1.5	13.8	1.2	1.6	9.3	0.7	0.9	12.8	1.0	1.4
	Ckg	(n=4) s.e.	39.1 3,0			11.3 0.7			13.6 0.5			12.4 0.3		
IV	Ap		40.0	1.0	1.2	12.3	0.8	1.2	12.8	0.8	1.0	13.5	1.1	1.3
	A2		33.8	0.9	1.1	10.7	0.7	1.2	10.2	0.6	0.9	12.4	1.0	1.3
	Bt		39.5	1.1	0.7	10.2	0.6	0.6	17.3	1.1	0.9	12.4	1.0	0.7
	Ckg	(n=2) s.e.	37.3 0.6			15.9 2.1			16.0 0.6			12.5 0.2		
V	Ap		34.7	0.9	1.4	9.8	0.6	1.3	7.7	0.5	0.8	15.6	1.1	1.3
	Et		23.5	0.6	1.1	6.9	0.4	1.0	7.2	0.5	0.7	14.3	1.0	2.1
	Bt		49.5	1.3	0.8	16.9	1.1	0.9	20.7	1.4	0.9	13.3	1.0	0.7
	Ck	(n=2) s.e.	39.3 0.9			15.6 3.3			14.3 0.8			13.6 0.3		

cont. Table 6

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
VI	Ap		30.0	0.9	1.5	7.2	0.6	1.2	5.6	0.4	0.8	14.8	1.1	2.4
	Et		20.0	0.6	1.1	5.7	0.6	1.1	4.5	0.3	0.7	14.1	1.1	2.5
	Bt		50.9	1.5	0.9	16.5	1.5	0.9	23.6	1.7	1.1	14.8	1.1	0.8
	Ck	(n=2) s.e.	33.6 0.3			11.3 0.4			14.0 0.6			13.4 0.5		
VII	Ap		42.5	1.1	0.9	11.5	1.0	0.8	14.6	0.9	0.9	16.5	1.1	1.1
	Bt1		49.5	1.3	0.9	12.6	1.1	0.8	15.9	1.0	0.8	17.5	1.2	1.0
	Bt2		45.6	1.2	0.9	14.2	1.2	0.8	17.5	1.1	0.8	18.2	1.2	1.0
	Ck	(n=2) s.e	37.5 0.6			15.3 0.4			11.7 0.5			14.9 0.3		
VIII	Ap		38.5	1.2	1.0	11.0	1.0	0.9	14.1	0.9	1.0	15.1	1.2	1.2
	Bw(t)1		42.8	1.3	0.8	13.3	1.2	0.8	16.8	1.1	0.9	13.6	1.1	0.8
	Bw(t)2		42.1	1.3	0.8	14.0	1.3	0.9	21.8	1.5	1.1	13.9	1.1	0.8
	Ck	(n=2) s.e.	32.8 2.1			11.0 0.7			15.0 1.6			12. 0.05		
IX	Ap		39.0	1.0	1.2	12.3	1.0	1.2	12.5	0.7	1.0	15.4	1.3	1.4
	Bw(t)1		45.0	1.2	0.8	14.6	1.2	0.8	19.9	1.2	0.9	14.0	1.2	0.7
	Bw(t)2		44.7	1.2	0.8	15.3	1.3	0.9	23.4	1.4	1.2	15.0	1.3	0.9
	Ck	(n=3) s.e.	37.1 0.9			11.9 0.3			16.6 0.5			11.7 1.1		

DI – Index of distribution in soil profile calculated from the average content of metal in parent material to the content of metal in analyzed horizons;
EF – Enrichment factor; AM – arithmetic mean;
s.e. – standard error.

Table 7

Content of Cr, Mn (mg kg^{-1}), and Fe, Ti (g kg^{-1})

No	Horizon	AM / s.e.	Cr	DI	EF	Mn	DI	EF	Fe	DI	Ti	DI	EF
1	2	3	4	5	6	7	8	9	10	11	12	13	14
I	Ap		3.2	0.7	0.8	335.4	1.1	1.4	12.6	0.8	1.0	0.8	1.0
	A2		3.2	0.7	0.7	304.2	1.0	1.2	13.9	0.9	1.3	1.0	1.2
	Ckg	(n=3) s.e.	4.3 0.5			300.8 20.3			16.1 0.5		1.3 0.0		
II	Ap		3.9	0.5	0.9	290.5	0.9	1.2	12.6	0.8	1.3	0.8	1.3
	A2		4.9	0.9	1.1	302.5	1.0	1.2	12.9	0.8	1.2	0.7	1.2
	AB		5.2	0.9	1.0	303.4	1.0	1.0	16.5	1.0	1.3	0.8	1.0
	Bt		5.9	1.0	0.9	298.2	1.0	0.8	19.9	1.2	1.3	0.8	0.8
	Ckg	(n=3) s.e.	5.7 0.2			306.9 39.3			16.6 1.1		1.6 0.2		
III	Ap		5.6	0.8	1.4	252.2	0.8	1.1	11.8	0.7	1.1	0.9	1.2
	A2		5.9	0.9	1.5	252.5	0.8	1.1	11.8	0.7	1.1	0.9	1.2
	Ckg	(n=4) s.e.	6.8 0.1			333.4 36.9			16.9 1.7		1.2 0.04		
IV	Ap		7.5	1.1	1.7	308.0	1.1	1.2	13.4	0.8	1.2	0.8	1.1
	A2		6.4	1.0	1.6	307.9	1.1	1.3	12.3	0.7	1.2	0.8	1.2
	Bt		9.0	1.4	1.2	340.6	1.2	0.8	21.8	1.3	1.3	0.9	0.8
	Ckg	(n=2) s.e	6.5 1.5			290.6 80.7			17.1 0.5		1.4 0.05		
V	Ap		4.1	0.7	1.2	265.5	0.8	1.4	10.0	0.6	1.1	0.8	1.4
	Et		4.0	0.7	1.4	298.0	0.9	1.8	8.8	0.5	1.3	1.0	1.9
	Bt		6.7	1.3	0.8	307.8	0.9	0.7	24.2	1.4	1.6	1.2	0.8
	Ck	(n=2) s.e.	6.0 0.1			345.3 16.6			16.8 0.8		1.3 0.05		

cont. Table 7

1	2	3	4	5	6	7	8	9	10	11	12	13	14
VI	Ap		4.0	0.8	1.5	295.3	1.1	2.0	7.9	0.5	1.1	0.8	1.8
	Et		3.9	0.8	1.7	191.0	0.7	1.4	7.1	0.4	1.2	0.9	2.1
	Bt		6.0	1.3	0.8	347.5	1.4	0.8	23.8	1.5	1.6	1.2	0.9
	Ck	(*n*=2) s.e.	4.8 0.2			254.8 11.9			16.1 0.5		1.3 0.05		
VII	Ap		6.4	1.2	1.0	356.2	0.9	1.0	18.6	1.1	1.2	0.9	0.8
	Bt1		9.1	1.7	1.3	451.2	1.2	1.1	21.5	1.2	1.6	1.2	0.9
	Bt2		7.4	1.4	0.9	412.3	1.1	0.9	23.8	1.4	1.7	1.3	0.9
	Ck	(*n*=3) s.e.	5.2 0.2			384.0 2.1			17.2 0.2		1.3 0.05		
VIII	Ap		4.8	1.1	0.9	274.2	1.1	0.9	15.6	1.0	1.3	1.0	1,1
	Bw(t)1		5.3	1.2	0.8	250,8	1.0	0.6	21.2	1.4	1.4	1.1	0.8
	Bw(t)2		5.1	1.2	0.6	311.1	1.2	0.8	21.6	1.4	1.7	1.3	0.8
	Ck	(*n*=2) s.e.	4.5 0.05			258.9 22.2			15.0 0.0		1.3 0.05		
IX	Ap		4.5	0.8	1.0	296.7	1.0	1.1	13.9	0.8	1.4	1.0	1.3
	Bw(t)1		5.8	1.0	0.7	267.2	0.9	0.8	23.5	1.4	1.7	1.2	0.9
	Bw(t)2		5.8	1.0	0.8	317.7	1.0	0.8	21.8	1.3	1.7	1.2	1.0
	Ck	(*n*=3) s.e.	5.6 0.3			300.9 8.0			16.8 0.1		1.4 0.0		

DI – Index of distribution in soil profile calculated from the average content of metal in parent material to the content of metal in analyzed horizons;
EF – Enrichment factor; AM – arithmetic mean;
s.e. – standard error.

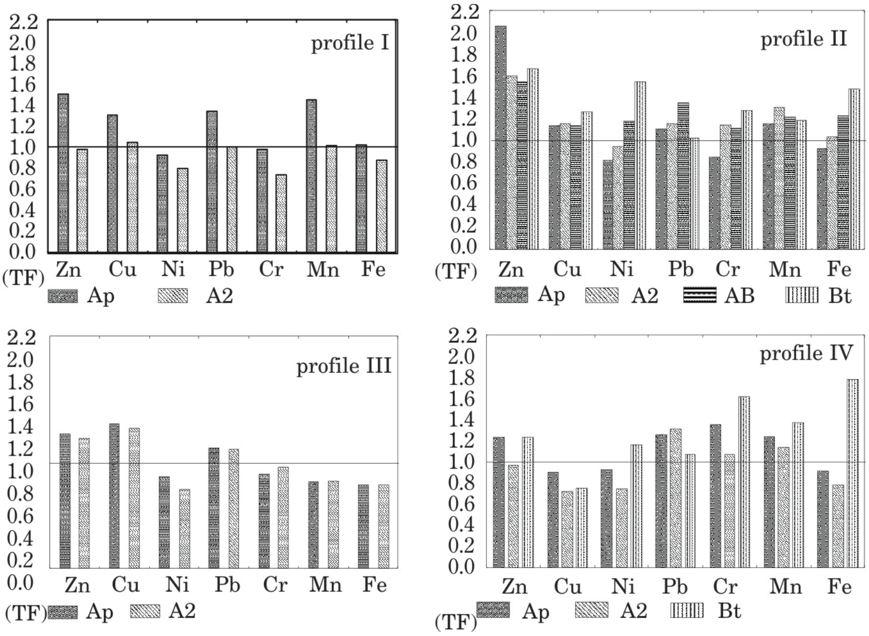

Fig. 2. Transfer factor (TF) calculated for Phaeozems

Table 8

Metal content and selected statistics for parent material of arable soils from the Inowrocławska Plain

		Zn	Cu	Ni	Pb	Cr	Mn	Fe	Ti
		(mg kg^{-1})						(g kg^{-1})	
Glacial till (n=23) Phaeozems Luvisols Cambisols	AM	40.6	12.6	14.3	12.9	5.5	309.9	16.5	1.4
	median	38.1	12.1	13.6	12.7	5.4	316.9	16.6	1.3
	SD (σ)	8.66	2.33	1.74	1.47	1.04	57.1	1.58	0.16
	upper limits the mean + 2σ range	57.9	17.3	17.8	15.8	7.6	424.1	19.7	1.7

AM – arithmetic mean, SD (σ) – standard deviation

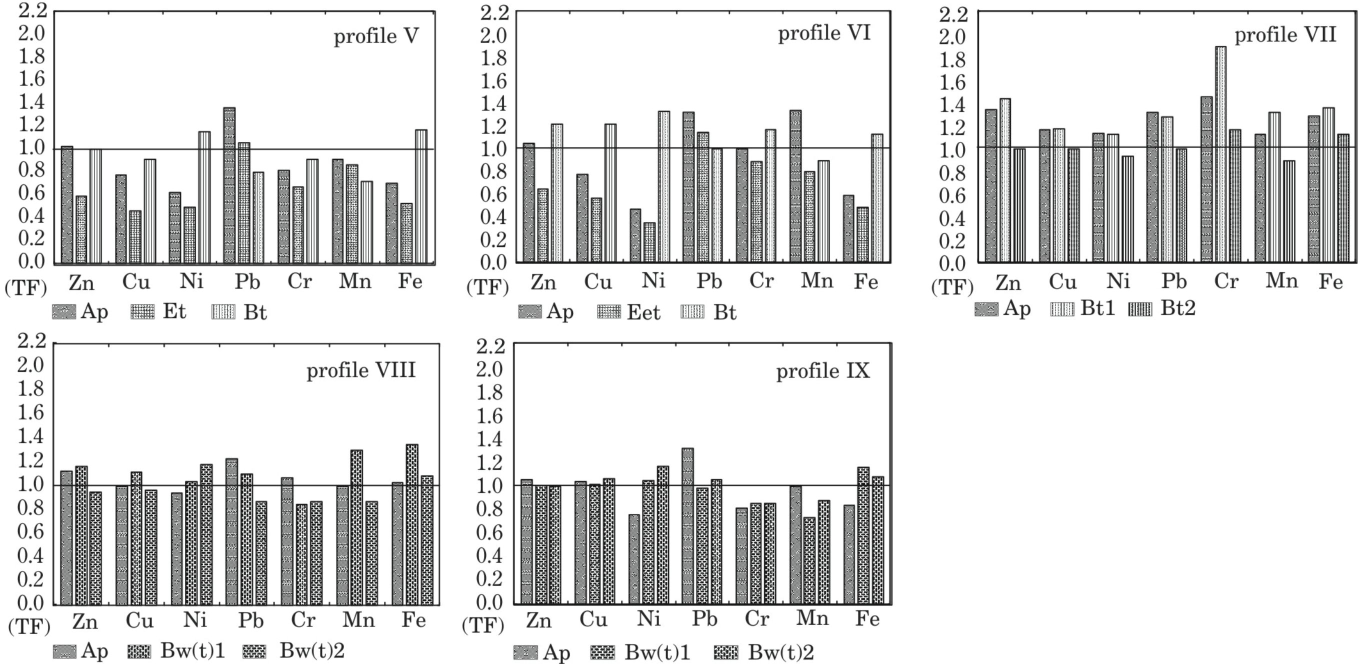

Fig. 3. Transfer factor (TF) calculated for Luvisols (profiles V, VI, VII) and Cambisols (profiles VIII, IX)

CONCLUSIONS

1. The distribution of Ni, Cr, Cu, Mn and Fe in the soil profiles must be the effect of pedogenic factors, however in the case of Zn and Pb, there was observed their tendency to accumulation in the humus horizons as a result of anthropogenic inputs.

2. The pedogenic formation of Fe oxides seems to be a factor determined the distribution of trace metals in the depth of soil profile. The distribution of pedogenic Ni, Cu, Cr and Mn was influenced by the specific adsorption of metals on Fe oxides. The results indicate that metals were bound more strongly to iron oxides then to the organic matter.

3. The distribution of metals in the soil profiles was most affected by the content of clay fraction, which was confirmed by the statistical analysis.

4. The content of Zn, Cu, Ni, Pb, Cr, Mn and Fe, Ti was defined as the content of the local background: 40.6; 12.6; 14.3; 12.9; 5.5; 309.9 (mg kg^{-1}) and 16.5; 1.4 (g kg^{-1}), respectively. A long-term agricultural use of soils in the Inowrocławska Plain resulted in a slight increase in the Pb, Zn, Cu content in comparison with the geochemical background.

5. The results confirm the importance of determining background concentrations locally. With the knowledge of the natural content of elements in the parent material, assumed as the geochemical background, one can evaluate the degree of contamination of topsoil.

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