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# CHANGES OF CHOSEN CHEMICAL ELEMENTS CONCENTRATION IN ALLUVIAL SEDIMENTS: AN EXAMPLE OF THE LOWER COURSE OF THE OBRA RIVER (WESTERN POLAND)

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**Keywords**: Chemical elements, alluvial deposits, the Obra River.

**Abstract**: Research concerning chemical constitution of alluvial sediments was done in the lower course of the Obra River (Western Poland). The fragment of vertical profile, which consisted of various alluvial sediments (fine sands, peats and sandy silts) was chosen for detailed analysis. Main research problem was to determine if lithology and chemical constitution of alluvial deposits are interconnected in a distinct way within studied section of the Obra river valley, and if changes of chemical elements concentration could be used to illustrate depositional processes which take place in river bed and floodplain. Concentrations of Fe, Mn, Cu, Zn, Ca, Mg and K were determined in collected sediment samples. Investigated changes of chemical elements concentration show that there is a distinct border between the organic sediments, which mark the place of former functioning of the Obra river bed, and sandy silts, which were deposited within floodplain during floods. Besides, dependence between lithologic variability of alluvial sediments and their chemical constitution was observed. However, this dependence is not clear in some cases. The authors concluded that it is necessary to use statistic analyses to define connection between lithology and chemical constitution of alluvial deposits (distinguishing geochemical groups of alluvial sediments).

## INTRODUCTION

Studies regarding Late-glacial and Holocene sediments concern mainly the deposits, which were accumulated in lakes [11, 24, 29, 30]. The research works, which referred to chemical constitution of sediments, were done in the areas polluted with heavy metals originating from mine industry [10, 15, 17, 19] which were entrained to transport in a river bed during extreme events (floods, landslides) [27, 28]. The authors of the mentioned above research works tried to distinguish sedimentation periods, which took place before, during and after intensive mining exploitation of researched areas. They found out that it is difficult to achieve this goal because of secondary migration of investigated metals to the sediments, which had no such contaminants before. They also noted that the minerals, which contained these metals, were subjected to disintegration or metamorphosis [13]. Other research [28] pointed to very important role of floodplain in periodic accumulation of chemical elements together with sediment during flood and repeated entraining to transport during next such event. The authors demonstrated that even 50% of chemical compounds transported annually in river bed cross-section can be deposited within floodplains as in the case of the Aire and the Swale rivers (Great Britain) [28]. Other researchers [26] paid attention to various sources of origin of increased concentrations of zinc, lead, copper and cadmium in the Subernarekha River (India). In the upper course of the river, the investigated metals originated from natural sources (valley bedrock) and in the lower course, from industrial pollution [26].

This paper presents the first part of the study regarding the determination of connections between lithology and chemical constitution of alluvial sediments. In the second part of the study [23] an attempt was made to define these connections by distinguishing geochemical groups of alluvial sediments using cluster analysis.

Main research problem was to determine whether lithology and chemical constitution of alluvial sediments are connected within studied section of the Obra river valley and, whether changes of chemical elements concentration could be used to illustrate depositional processes, which take place in the river bed and floodplain. The following research tasks were done:

1. Lithology of alluvial deposits was recognized to choose vertical profiles, which geologic structure of which is particularly variable.
2. Analyses of chosen chemical elements concentration were done to determine connections between lithology and chemical constitution of alluvial sediments.
3. Analysis of Fe/Mn, Fe/Ca, Ca/Mg and Cu/Zn ratios was done to determine changes of oxidation/reduction conditions in alluvial deposits. On the basis of the analysis, an attempt was made to identify the dominant type of denudation within studied area.

The problem of concentration changes of chemical elements in alluvial deposits was a part of research concerning the lower course of the Obra river valley (Western Poland). The reasons of choosing this area were the following:

- the Obra River is the biggest water course situated between the Warta and the Odra rivers (Fig. 1), which flows through the middle and western part of Wielkopolska lowland;
- specific hydrological regime, which is influenced by the presence of lakes in the course of the Obra River. The lakes smooth the amplitude of water stages, discharges and floods [1, 4, 6]. The Obra River has a regular rhythm of water stages fluctuations. According to Dynowska [8] this water regime is counted among temperate regimes with spring flood and groundwater-rainfall water supply.

## RESEARCH AREA

The study concerning changes of chemical elements concentration in alluvial deposits was done in the lower course of the Obra River, which flows through a geographic region named the Depression of Obra (Fig. 1). This is a concave form of landscape spreading from north-west to south-east. Detailed characteristics of this area relating to geologic structure, geomorphology and waters are presented in other publications [2, 7, 25].

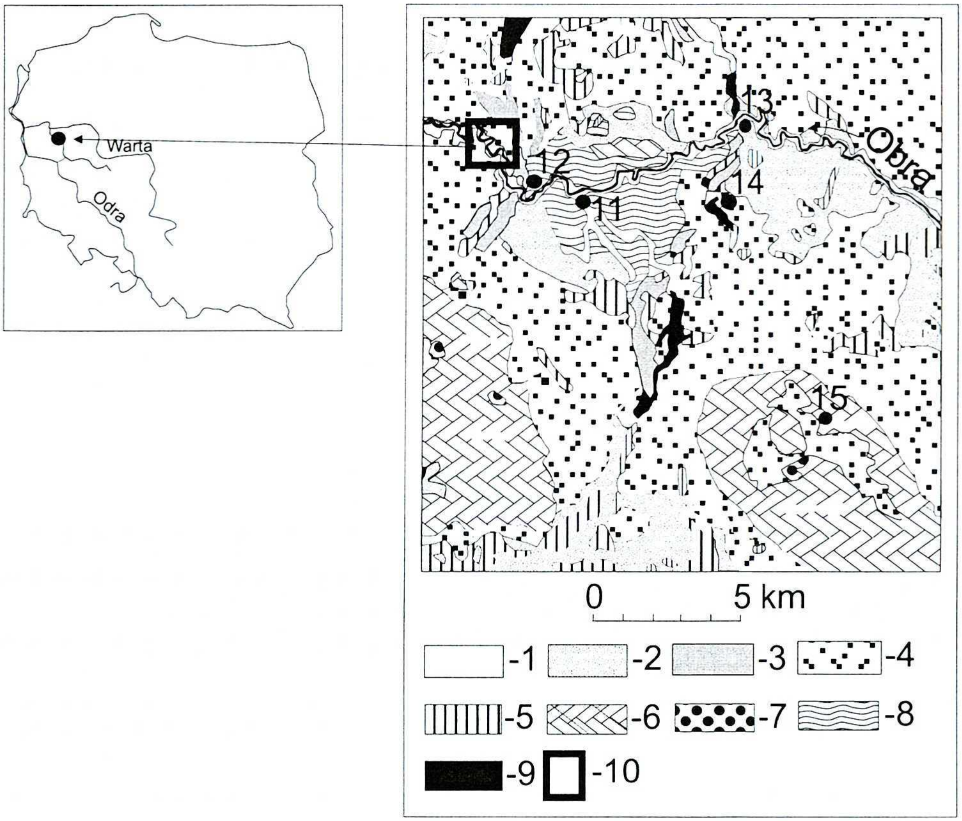


Fig. 1. Surface sediments geologic map. Localization: Świebodzin [18]; 1 – river sands, silts and gravels (Holocene), 2 – river sands, silts and gravels (Północnopolskie glacial period, Pomeranian phase), 3 – sands and gravels in eskers, 4 – fluvioglacial sands and gravels (Północnopolskie glacial period, Poznańsko-dobrzyńska phase), 5 – peats (Holocene), 6 – basal till or its residuum, 7 – sands, gravel and boulders of terminal moraines, 8 – lacustrine silts, sands and loams, 9 – rivers and lakes, 10 – detailed research area; main towns and villages: 11 – Międzyrzecz, 12 – St Wojciech, 13 – Żółwin, 14 – Bobowicko, 15 – Bukowiec

Detailed research was done near St Wojciech village, 3.5 km north-west of the town of Międzyrzecz (Fig. 1). The Obra is a meandering river within the chosen section of the valley. Hydro-technical works, which took place in the past, were limited in this area and did not change neither the river bed geometry nor the structure of alluvial sediments. The Obra River formed its valley in glacial sediments represented by glacial till and fluvioglacial fine sands, which can be seen in exposures occurring in concave riverbanks.

## RESEARCH METHODS

Tube sample borings were done in the Obra valley floor in five geological cross-sections (Fig. 2A) to choose vertical profiles, the geologic structure of which is particularly variable. The fragment of vertical profile from geologic cross-section no 1 (Fig. 2A) was chosen for detailed analysis. There are fine sands in the base of the profile (Fig. 2B) followed by peat sediments with numerous, 1–2 cm thick inserts of fine sands in its middle part. At the top of the profile, there are sandy silts (Fig. 2B).

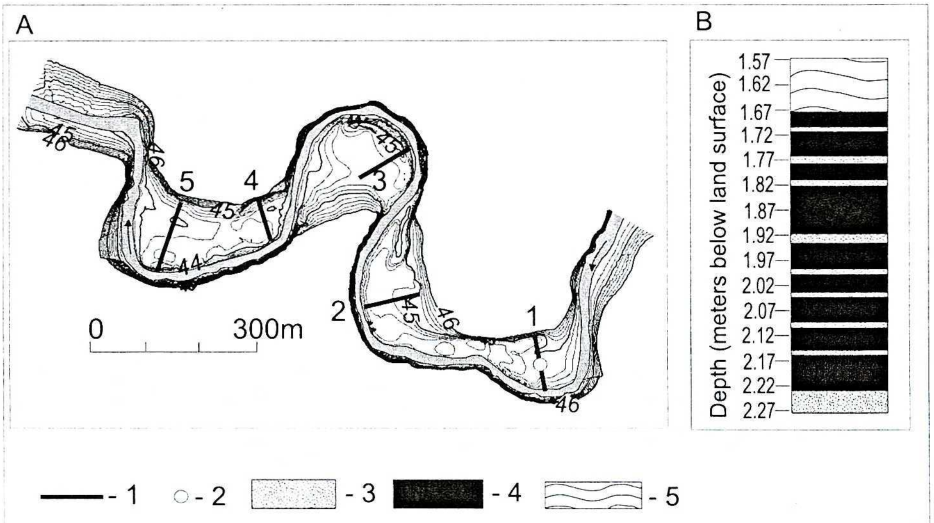


Fig. 2. Research area with marked location of geological sections and position of investigated vertical profile (A), and lithological variability of alluvial sediments forming investigated fragment of vertical profile (B); 1 – location of geologic sections, 2 – location of investigated vertical profile, 3 – fine sands, 4 – peats, 5 – sandy silts

A variable geological structure makes it possible to analyze changes of particular chemical elements concentration depending on lithologic variability of alluvial deposits. There are sediments within the fragment of investigated vertical profile, which have relatively high filtration coefficient (fine sands), and organic deposits, where migration of most macro- and microelements can be limited [20]. These sediments contain colloidal, mineral and humus substances, which form stable bonds with migrating substances and chemical elements. Peat sediments are the example of geochemical barrier of adsorptive type [20].

To determine changes of chosen chemical elements concentration in alluvial sediments, 71 samples were taken from the fragment of vertical profile. The samples were collected in 1 cm intervals. Next, the analyses of Fe, Mn, Zn, Cu, Ca, Mg and K were done. Changes of these elements concentration are interpreted in literature as indicators of particular type of environment (for example: reductive environment) or dominant type of denudation [3, 29]. The concentrations of particular chemical elements were defined using atomic absorption spectrometry method. The measurements were done using AAnalyst 300 Perkin Elmer spectrometer (atomization in air-acetylene flame after previous wet mineralization and dilution of the sample in concentrated nitric acid and hydrogen peroxide).

For each of the samples the following ratios were calculated:

Fe/Ca – proportion used in the studies concerning sediments deposited in lakes [29], which provide information regarding the water level changes. Its high values are interpreted as illustration of relatively low water level in lakes and occurrence of reductive conditions [29]. In the case of studies concerning floodplain sediments, the proportion might indicate periods with numerous floods events (and, in the case of the Obra river valley, increased concentration of Ca [22]) and periods joined with more stable discharges (an increase of reductive conditions and concentrations of Fe).

Ca/Mg – refers to determining the type of denudation. Ca/Mg proportion can be used as indicator of domination of mechanic denudation (Ca < Mg) or chemical denudation (Ca > Mg) [3].

Fe/Mn and Zn/Cu – indicators of changes of oxidation/reduction conditions.

The fragment of investigated vertical profile was divided into the following three parts to analyze changes of chosen chemical elements concentrations:

- bottom part: fine sands, which are the result of point bar accumulation;
- middle part: peat sediments with inserts of fine sands. In the studied section of the Obra river valley, agglomerations of organic deposits occur in the places of former functioning of the river bed. The inserts of fine sands illustrate intensive flood events, which took place in the past [22];
- top part: sandy silts, which are the result of vertical accretion in the area of floodplain during floods.

The division presented above shows that the bottom part of the profile represents river bed sediments and the remaining two parts – the deposits, which were accumulated in the nearest vicinity of the river bed or in the area of floodplain.

It should be noted that the presented analysis refers only to the fragment of single vertical profile within studied section of the Obra river valley. Only preliminary conclusions regarding the research problems presented above can be suggested on the basis of this study.

## CHANGES OF THE CHEMICAL ELEMENTS CONCENTRATIONS IN THE BOTTOM PART OF THE PROFILE

Sediments of the bottom part of the profile, represented by fine sands, are the result of point bar accumulation process, which was especially intensive during period of low water stages and relatively small intensity of lateral erosion [22]. Ca and Mg, the elements joined with mineral deposits, have the biggest concentrations here. High content of Ca (maximum 22.4 $mg \cdot g^{-1}$, Fig. 3) is the result of its concentrations in glacial till, which underlies alluvial sediments. Ca is the chemical element which easily migrates in water environment. Mg (maximum 8.45 $mg \cdot g^{-1}$, Fig. 3) is much less susceptible to migration in water and biological cycle. This element is much more related to sorption complex of soils and wastes. Besides, Mg is joined with clay grain-size fraction and increased content of silica [3]. The concentrations of K were also slightly increased (above 300 $\mu g \cdot g^{-1}$, Fig. 3). This chemical element, as well as Mg, in the case of lacustrine sediments is connected to clay grain-size fraction [21] and silica content. Besides, it is inversely related to organic matter content [3, 29].

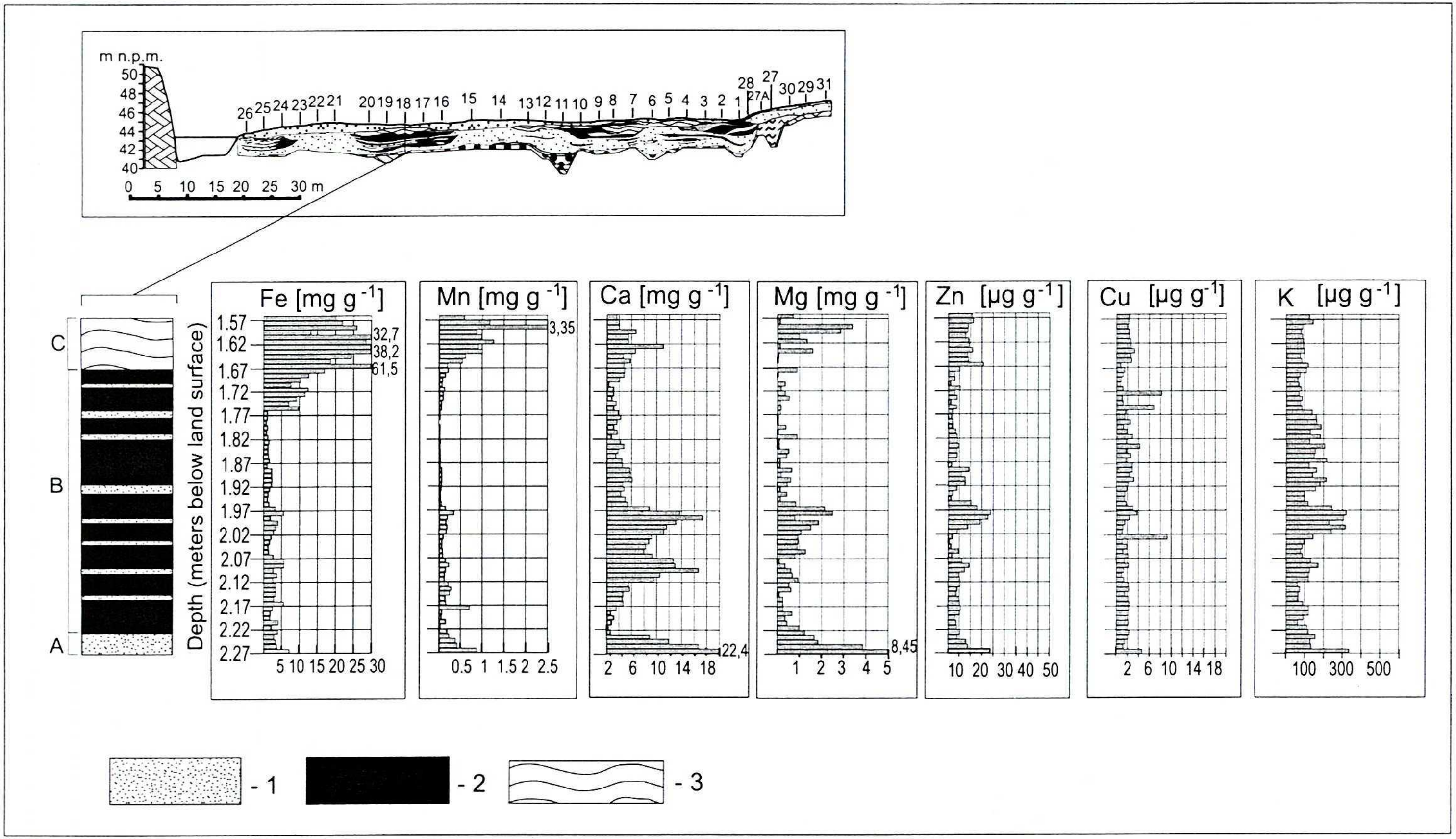


Fig. 3. Changes of concentration of chosen chemical elements in alluvial sediments of the Obra river valley (geologic section no 1, fragment of vertical profile no 18); 1 – fine sands, 2 – peats, 3 – sandy silts, A – bottom part of investigated fragment of vertical profile, B – middle part, C – top part; concentrations of Zn, Cu and K were presented in a scale 1000 times smaller than other chemical elements

## CHANGES OF THE CHEMICAL ELEMENTS CONCENTRATIONS IN THE MIDDLE PART OF THE PROFILE

The sediments, which are situated in the middle part of the profile, were accumulated during the period of frequent occurrence of flood events and significant influence of lateral rosion process. These deposits mark the place where the Obra river bed was functioning in the past [22]. Organic sediments were deposited in a lateral, stagnant water channel, which was formed in the vicinity of laterally migrating river bed during the period of high water stages [22]. Accumulation of the sediments in stagnant water within such channel or within inundated fragment of floodplain was accompanied with reductive conditions. The presented results (Fig. 3) show that there are two zones in the profile with strongly reductive environment. The first one is situated at the depth of 1.67–1.77 m below land surface and is marked with high concentrations of Fe and Cu, which indicate reductive environment with sulphuretted hydrogen. Fe/Mn proportion is also high here. Research done by McArthur (in: [12]) show that the environment of peat sediments is the place of iron hydroxides reduction. According to Borówka [3] and Salminen *et al.* [21], Fe has low ability to migrate in such environment because of precipitation of iron sulphur, which is difficult to dissolve.

The second zone, at the depth of 1.95–2.03 m below land surface, is characterized by high concentrations of Cu, Mn and Zn. Increased concentrations of Mn are situated at the depths of 2.18 m below land surface (0.7 $mg \cdot g^{-1}$) and 1.98 m below land surface (0.3 $mg \cdot g^{-1}$, Fig. 3). Mn usually occurs in lower concentrations than Fe, which is the result of low solubility of its salts [9]. Increased Mn concentrations are accompanied by high Fe contents (more than 5 $mg \cdot g^{-1}$). Presumably, there are reductive conditions with the presence of $H_2S$ at the depths mentioned above. Cu and Zn are also indicators of such environment [3, 14, 20]. Increased Cu concentrations were detected in peat deposits at the depth of 2.03 m b.l.s. (9.5 $\mu g \cdot g^{-1}$), 1.72 m b.l.s. (8.1 $\mu g \cdot g^{-1}$) and 1.77 m b.l.s. (7 $\mu g \cdot g^{-1}$) (Fig. 3). Zn content in peat sediments amounts 15–25 $\mu g \cdot g^{-1}$ at the depth of 1.95–2.00 m b.l.s. (Fig. 3). The proportions of Cu/Zn and Fe/Mn are also high here (Fig. 4). It should be noted that low values of Cu/Zn ratio do not always mean the lack of reductive conditions and important role of oxidative environment. This could happen in the case when Zn concentrations exceed Cu content and indicate the domination of reductive conditions (Zn creates hardly soluble bonds in such environment [14, 20]).

The inserts of fine sands within peat deposits are the traces of intensive flood events, which caused inundation of floodplain. When water level was falling down, the transported material was accumulated as 1–2 cm thick layers of sand deposits. Increased contents of Ca, Mg and K were observed in some of such mineral inserts (Fig. 3). In fine sand layers with high concentrations of Ca, increased concentrations of K were detected (maximum 2.5 $mg \cdot g^{-1}$, Fig. 3). However, increased contents of Mg and K also occur in peat deposits. This could be explained by increased content of mineral fraction in organic sediments. Such admixtures could be added to peats during floods of lesser magnitude. Besides, Mg and K could migrate vertically from the inserts of fine sands. When comparing concentration of Ca and Mg, it can be observed that the first of these two elements is characterized by much higher concentrations. According to Borówka [3] greater concentrations of Ca would suggest that chemical denudation is dominant within the studied area. Lower values of Ca/Mg ratio in most cases refer to fine sands in the profile (Fig. 4), which is the result of an increase of Ca and Mg content within inserts of sand deposits (Fig. 3). However, such raise concerns not only fine sands but it is also observed within peat sediments. This may be caused by greater content of mineral material in some peat layers. Besides, glacial till, which is situated beneath alluvial sediments, can also influence the greater concentrations of Ca because it contains $CaCO_3$ [22]. The area of the Obra river valley is supplied with ground waters originating from Lubuska moraine plateau [5]. It is possible that the compounds of Ca were being washed out from glacial till and later redeposited in alluvial sediments. Such processes are still active, especially during flood events when Ca concentrations increase together with water level [22].

## CHANGES OF THE CHEMICAL ELEMENTS CONCENTRATIONS IN THE TOP PART OF THE PROFILE

The top part of investigated profile consists of sandy silts, which are floodplain sediments. These deposits contain great amount of colloidal substances accumulated through decantation during flood events in stagnant waters within floodplain area. Distinct increase of Fe (maximum 61.5 $mg \cdot g^{-1}$), Mn (3.35 $mg \cdot g^{-1}$), Mg (3.4 $mg \cdot g^{-1}$) and Zn (21 $\mu g \cdot g^{-1}$) concentrations was observed here (Fig. 3). Such increase is illustrated by the highest in studied profile values of Fe/Mn and Fe/Ca ratios (Fig. 4). The biggest contents of Fe, Mn and Zn are usually present in mineral deposits enriched with colloidal substances [3, 21]. Research done by Liu *et al.* [16] has shown that heavy metals concentrations are 2–4 times greater in fine deposits than in the sediments enriched with coarser grain-size fractions. Similar results were achieved in the case of Pb, Zn, Cu, Ni and Cr concentrations in the deposits of the Mekhna River (Bangladesh) [12] where contents of these elements were much higher in silts than in sands.

Fe/Ca ratio also has maximum value (> 6) in the top part of the profile (Fig. 4). In the case of the deposits of the Obra river valley this proportion does not reflect water level changes in the past. Alluvial sediments are formed in the environment of much greater dynamics and variability than lacustrine sediments where Fe/Ca ratio can be used to reconstruct changes of water level [29].

Silts are the finest deposits present within studied section of the Obra river valley (mean diameter: 3 phi) [22]. In the top part of studied profile, rapid increase of concentration of chemical elements mentioned above (Fig. 3) marks the border between the environment of organic sediments, which were accumulated in the place where the Obra river bed was functioning in the past, and the environment of floodplain sediments.

## CONCLUSIONS

On the basis of the analysis of chosen chemical elements concentrations within investigated fragment of vertical profile, the following conclusions can be drawn:

1. In the studied fragment of the profile, there are two zones representing strongly reductive conditions with the content of $H_2S$ within peat deposits. They are situated at the depths of 1.67–1.77 below land surface and 1.95–2.03 m below land surface, and are characterized by increased contents of Fe, Mn, Cu and Zn. Reductive conditions in these two zones are strongly connected with the way of forming peat sediments. Peats were accumulated on wet area of floodplain or in a lateral, stagnant water

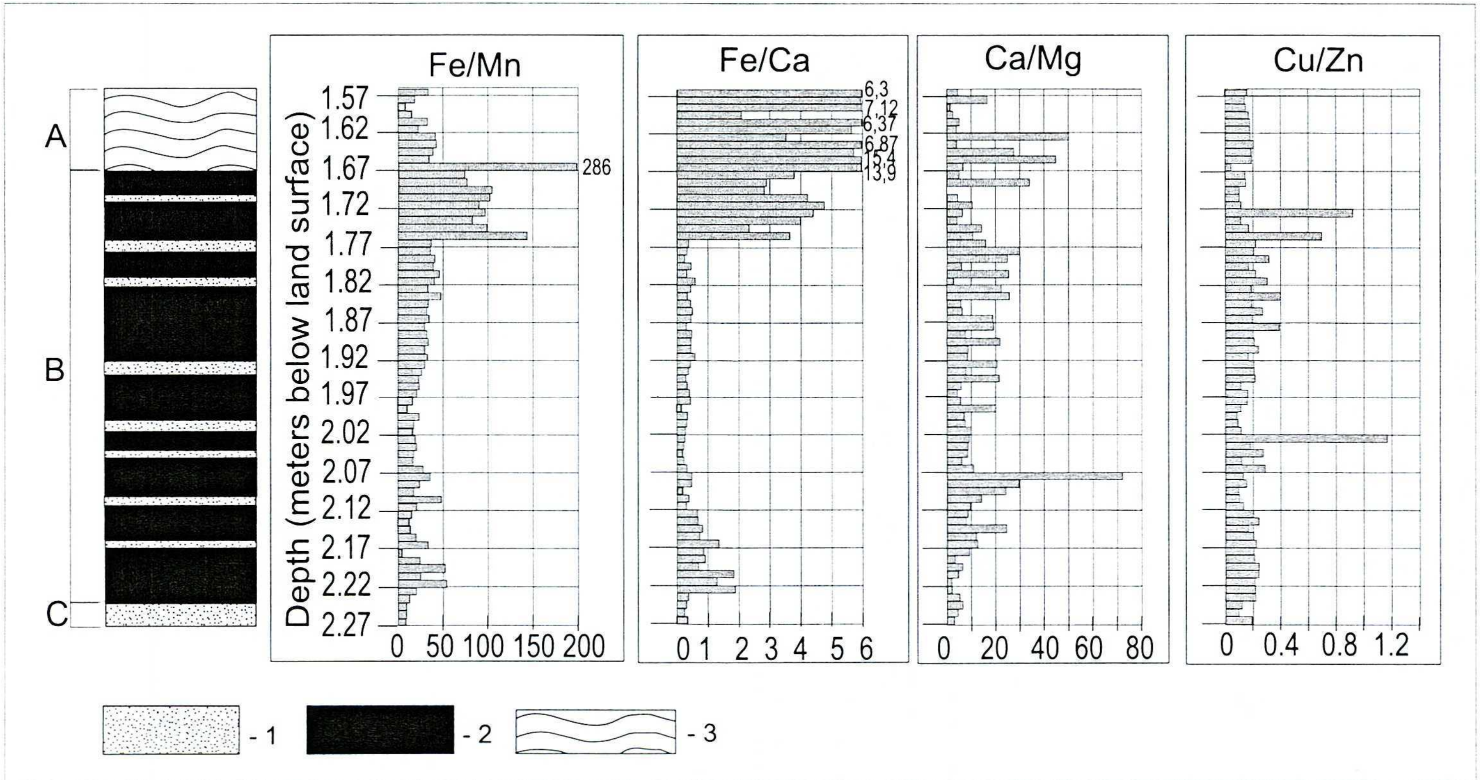


Fig. 4. Changes of Fe/Mn, Fe/Ca, Ca/Mg and Cu/Zn ratio regarding to alluvial sediments of the Obra river valley (geological section no 1, investigated fragment of vertical profile no 18); explanations are the same as at Fig. 3

channel, which was shaped by migrating Obra river bed during period of frequent flood events. It can be suggested that organic sediments mark the place where the Obra river bed was functioning in the past [22].

2. There is a distinct border between the environment of organic sediments, which fill the place of former river bed and the environment of floodplain represented by silt deposits (accumulated through vertical accretion during flood events within inundated fragment of floodplain). The border is marked with rapid increase of Fe, Mn, Mg and Zn concentrations (Fig. 3).
3. High values of Ca/Mg ratio show much greater contents of Ca in the profile. According to Borówka [3] this would suggest that chemical denudation is dominant within investigated section of the valley.
4. The dependence between lithologic variability of alluvial deposits and its chemical constitution is observable. There is increase of Ca, Mg and K content in the inserts of fine sands within peat deposits. These 1–2 cm thick sandy layers illustrate especially intensive flood events in the past [22]. However, it should be noted that increased contents of these chemical elements also occur in peat deposits. This may be caused by admixtures of mineral material in organic sediments.
5. On the basis of achieved results it is difficult to distinguish particular geochemical groups of alluvial deposits. Floodplain sediments (sandy silts) in the top part of the profile are the only exception (conclusion no. 2). Determining the dependence between lithology and chemical constitution of alluvial sediments can be done in more detailed way using statistical analyses.

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## ZMIANY KONCENTRACJI WYBRANYCH PIERWIASTKÓW CHEMICZNYCH W OSADACH ALUWIALNYCH: PRZYKŁAD DOLNEGO ODCINKA DOLINY OBRY

Badania składu chemicznego osadów rzecznych przeprowadzono w dolnym odcinku rzeki Obry 3,5 km na północny zachód od Międzyrzecza. Do analizy wybrano fragment profilu pionowego o zróżnicowanej litologii. Głównym celem badań było określenie, czy litologia i zmienność składu chemicznego osadów rzecznych są od siebie w istotny sposób uzależnione w badanym fragmencie doliny, i na ile wiarygodny zapis zmian zachodzących na obszarze zlewni rzecznej stanowi skład chemiczny osadów aluwialnych. W pobranych próbkach osadów określono koncentrację żelaza, manganu, miedzi, cynku, wapnia, magnezu i potasu. Wykazano, że zmiany koncentracji pierwiastków chemicznych wskazują na wyraźną granicę pomiędzy środowiskiem osadów organicznych wypełniających miejsce dawnego funkcjonowania koryta, a środowiskiem pozakorytowym reprezentowanym przez osady mułkowe. Ponadto w badanym fragmencie profilu zauważalny jest związek między zmiennością litologiczną osadów aluwialnych dna doliny Obry a ich składem chemicznym. Zależność ta nie jest jednak ścisła. Wskazano na konieczność wykorzystania analiz statystycznych w celu bardziej szczegółowego określenia związku między litologią i składem chemicznym osadów rzecznych (wydzielenie grup geochemicznych osadów).