ARCHIVES OF ENVIRONMENTAL PROTECTION

vol. 35 no. 1 pp. 87 - 94 2009

PL ISSN 0324-8461

GEOCHEMICAL GROUPS OF ALLUVIAL SEDIMENTS OF THE LOWER COURSE OF THE OBRA RIVER: AN EXAMPLE OF USING CLUSTER ANALYSIS

MARCIN SŁOWIK[1*], TADEUSZ SOBCZYŃSKI[2], ZYGMUNT MŁYNARCZYK[1]

[1] Adam Mickiewicz University, Department of Geographic and Geologic Sciences
ul. Dzięgielowa 27, 61-680 Poznań, Poland
[*] Corresponding author e-mail: slowikgeo@poczta.onet.pl
[2] Adam Mickiewicz University, Department of Chemistry
ul. Drzymały 24, 60-613 Poznań, Poland

Keywords: Cluster analysis, Ward's method, alluvial deposits, chemical elements, the Obra River.

Abstract: Research concerning changes of chosen chemical elements concentration in alluvial sediments was conducted in the lower course of the Obra river valley. The analyses of Fe, Mn, Cu, Zn, Ca, Mg and K concentration were done in a fragment of vertical profile, which was characterized by variable lithology. On the basis of statistical analysis (cluster analysis) an attempt was made to distinguish geochemical groups of alluvial sediments of the Obra river valley. Six geochemical groups, which represent reductive conditions within peat deposits, the environment of flood sediments (inserts of fine sands within peats and sandy silts in the top of the profile) and the environment of river bed sediments (fine sands in the bottom part of the profile), were singled out. Results of the study show that it is possible to distinguish the above mentioned depositional environments on the basis of variations of sediments' chemical constitution.

INTRODUCTION

The first part of the study [12] has shown that it was difficult to distinguish geochemical groups of alluvial sediments, which would represent particular types of depositional environment. In this paper, which presents results of the second part of the study, cluster analysis was used to single out geochemical groups of alluvial sediments. This analysis allows to combine together particular objects or features on the basis of similarity function [4]. The aim of grouping is to obtain n groups of objects in such a way that the loss of information during grouping process in minimized. The first step is joining two objects (features), which results in the smallest square distances increase between the two grouped objects (features) [1]. Another stage is checking if the third object can be included in a 2-element cluster formed in the first stage of the analysis or can form another cluster. The procedure is repeated until the moment when all objects and clusters of objects are connected together [13]. Connection of objects or features is done using one of agglomeration methods [13] and matrix of square distances. Each cluster refers to definite level described by Euclidean distance [4].

Cluster analysis is widely applied in various studies concerning medical problems [9, 10, 15] or regarding the choice of variables to neural network model [14]. In the case of natural studies, this method was used to distinguish types of meadow plants [7]. Cluster analysis was also applied to sort out climate types in the area of Saudi Arabia [1] and Europe [3] using the function which helped to establish optimal number of achieved clusters [3]. Another study [2] concerned intensity of erosion and mass movements. Using cluster analysis, interactions between river network density, type of vegetation and land use were shown. Besides, the units of land use type, which are endangered with erosion of various intensity, were sorted out [2]. In the case of research regarding intensity of soils erosion using Cs^{137} radionuclide method, cluster analysis was used to distinguish among soil erosion classes depending on lithology, location of studied profiles and slope shape [8]. The analysis was also applied to determine the dependence between soil type and shape of slopes [16].

In the second part of the research, which is presented in this paper, the main study problem was to define more closely the connections between type of sediment, its chemical constitution and properties of depositional environment. The following research tasks were done:

1. Determination of variability of alluvial deposits lithology.
2. Analyses of chosen chemical elements concentration in alluvial sediments of investigated fragment of vertical profile.
3. Distinguishing geochemical groups of the Obra river valley alluvial deposits using cluster analysis.

Description of research area and figures illustrating its localization were presented in the first part of presented study [12].

RESEARCH METHODS

A fragment of the vertical profile from the middle part of geologic cross-section no. 1 was chosen for detailed analysis (Fig. 2A in [12]). The deposits of the profile, the way of samples collection and laboratory analyses were described in the first part of the study [12]. Variable geologic structure makes it possible to analyze changes of particular chemical elements concentration depending on lithologic variability of alluvial deposits. Within the fragment of investigated vertical profile, there are sediments, which have relatively high filtration coefficient (fine sands), and organic deposits, where migration of most macro- and microelements can be limited [6]. Concentrations of the following chemical elements were subjected to detailed analysis: Fe, Mn, Cu, Zn, Mg, Ca and K.

Geochemical groups of the Obra river valley alluvial sediments were distinguished on the basis of concentration changes of particular chemical elements in the studied fragment of vertical profile (Fig. 2). The groups were singled out using cluster analysis (Ward's method, 1-r Pearson's distances) [4, 13] (Fig. 1). Ward's method is different from other agglomeration methods. It uses variance analysis to determine distances between clusters. It also assumes minimal square distance between each two clusters, which are formed during particular stages of analysis. It is thought to be one of the best agglomeration techniques [5] and is frequently used. In the simulation, which was done by Mangiamelli *et al.* [5], 252 datasets were tested using all agglomeration techniques. Ward's method gave one of the best results in joining objects into logically ordered clusters.

Before the analysis, the input data were standardized to eliminate considerable difference between values of particular variables (chemical elements concentrations). The values were standardized using formula:

$$\frac{x_i - \bar{x}}{\delta},$$

where:

x_i – value of variable x_i,

$\bar{x}$ – mean value of variable,

δ – standard deviation.

The following variations of chemical elements concentrations were taken into account when forming geochemical groups:

1. Distinct increase or decrease of chemical element concentration.
2. Referring chemical constitution of alluvial sediments to its lithology within each distinguished group of clusters. Recognition of geologic structure of analyzed profile makes it possible to describe processes, which formed particular types of sediments. Knowledge concerning properties of depositional environment may be useful to analyze the way of accumulation of particular chemical elements in various types of deposits.

Six geochemical groups were distinguished. Mean value of each chemical element was calculated within each group. The obtained results are presented in Table 1.

RESULTS OF THE STUDY

The following classification geochemical group of alluvial sediments of the Obra river valley was done:

I – geochemical group of fine sands and peats containing inserts of fine sands, characterized by increased Ca, Mg and K concentrations (Fig. 1)

The sediments, which belong to this group, are situated in the bottom part of the studied fragment of vertical profile at depth 2.24–2.27 m below land surface (fine sands) and 2.04–2.12 m b.l.s. (peats with inserts of fine sands) (Fig. 2). This geochemical group is featured with high concentrations of Ca (mean concentration: 10.88 $mg \cdot g^{-1}$, maximum: 22.4 $mg \cdot g^{-1}$) and distinct variations of Mg (maximum concentration: 8.45 $mg \cdot g^{-1}$) and K content (mean concentration 131.6 $\mu g \cdot g^{-1}$, Tab. 1). Mg and K are accumulated within colloidal elements of sand deposits. Ca is one of the main chemical components of the Obra river valley, which is the result of high Ca concentrations in glacial till beneath alluvial

Table 1. Mean concentrations of studied chemical elements in distinguished geochemical groups

Chemical element	Fe	Mn	Ca	Mg	Zn	K	Cu
Concentration units	[$mg \cdot g^{-1}$]	[$mg \cdot g^{-1}$]	[$mg \cdot g^{-1}$]	[$mg \cdot g^{-1}$]	[$\mu g \cdot g^{-1}$]	[$\mu g \cdot g^{-1}$]	[$\mu g \cdot g^{-1}$]
Group I	3.25	0.217	10.88	1.59	11.44	131.6	1.78
Group II	3.08	0.16	9.6	1.37	18.69	222.71	2.5
Group III	1.72	0.061	4.74	0.476	10.06	180.8	2.14
Group IV	4.48	0.107	3.38	0.631	9.51	101.64	3.88
Group V	5.31	0.234	5.05	0.937	11.29	69.74	2.16
Group VI	22.55	0.695	4.49	0.889	13.25	92.27	1.9

sediments [11]. Deposits belonging to this group were accumulated in most part during formation of meander point bar in period of low water levels [11] and represent river bed depositional environment.

II – geochemical group of peat deposits with inserts of fine sands, characterized by increased concentrations of Ca, Mg and K, and high contents of Zn and Cu (Fig. 1)

Distinguished geochemical group is situated at the depth of 1.96–2.00 m below land

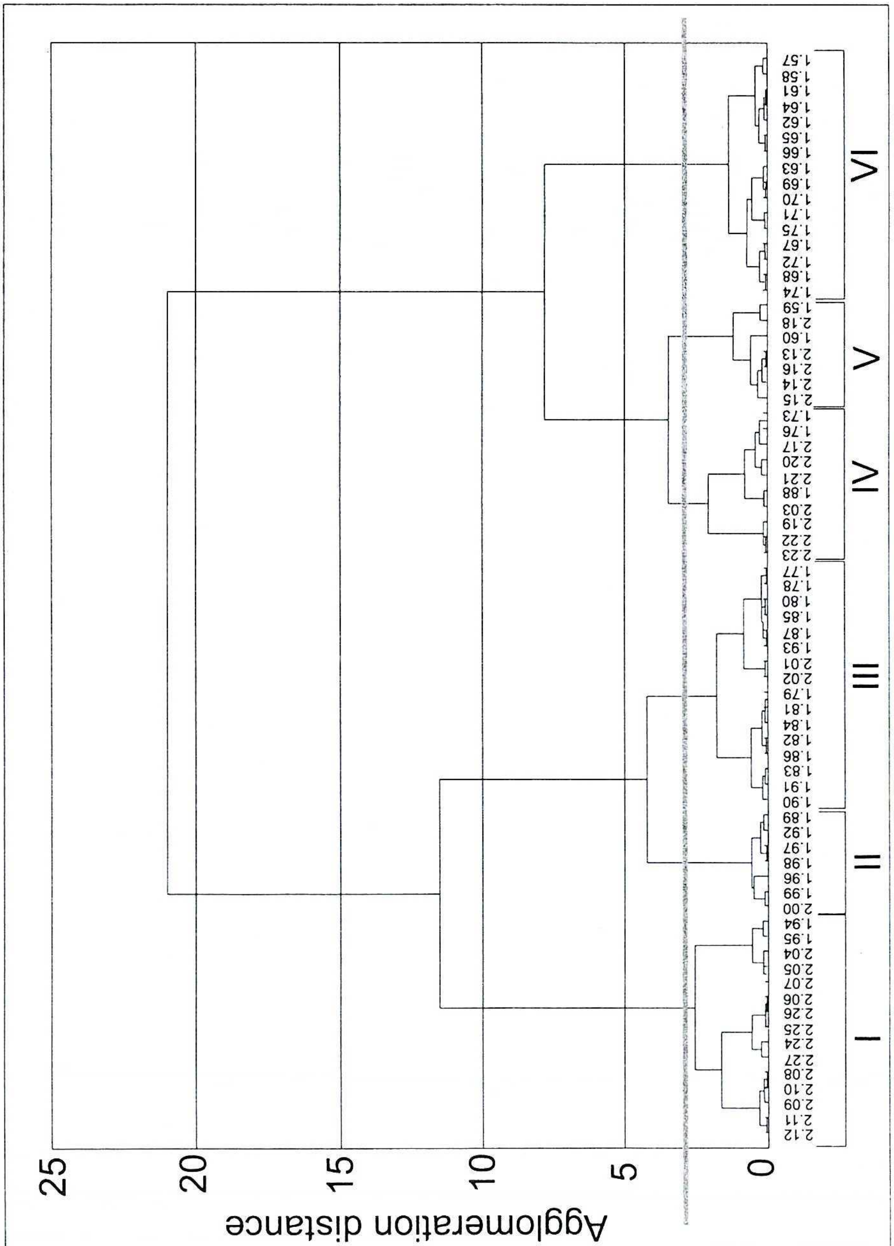

Fig. 1. Geochemical groups of alluvial deposits of the Obra river valley distinguished by using cluster analysis (Ward's agglomeration method, 1-r Pearson's distances, [4, 13]), I – VI – geochemical groups

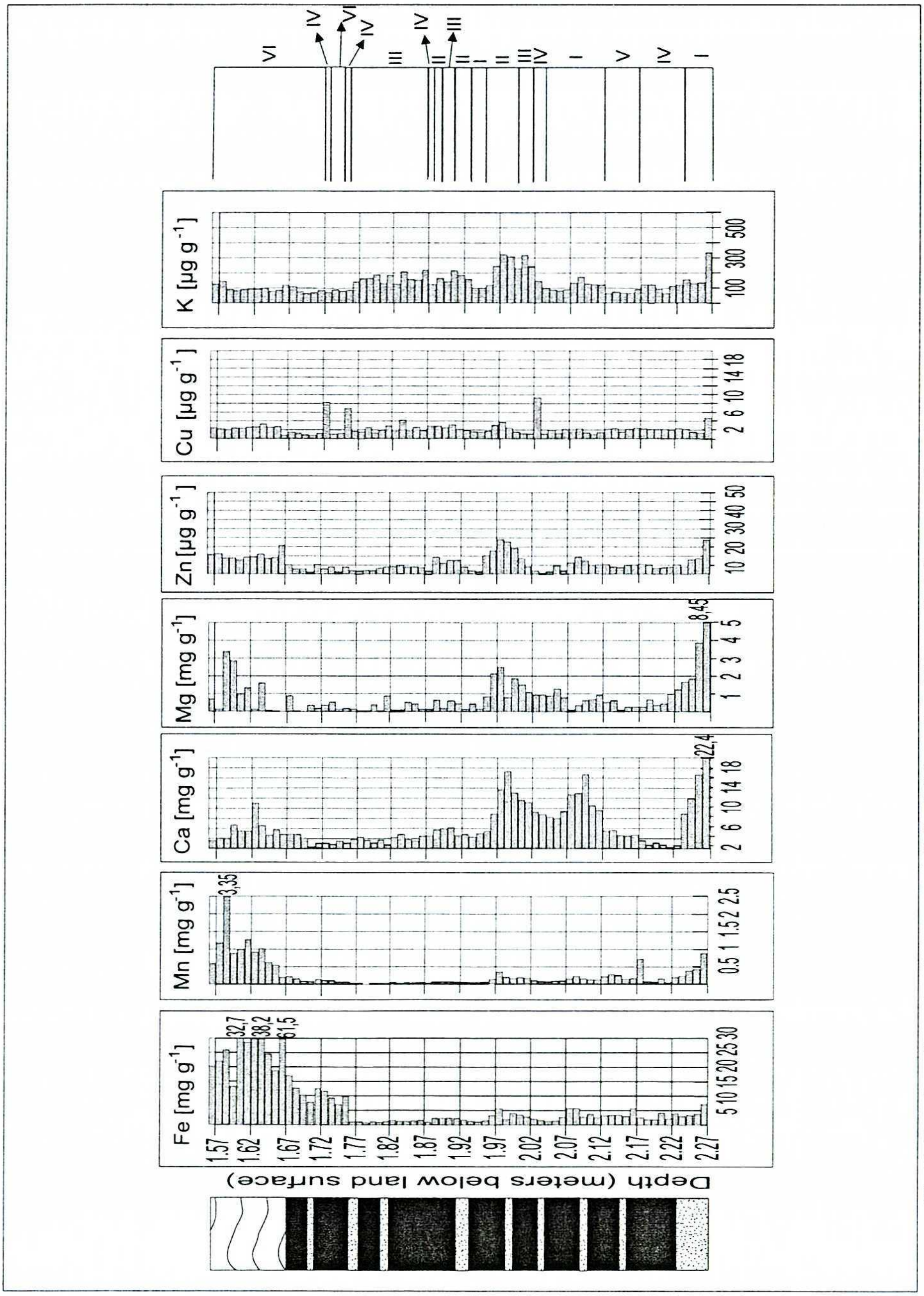

Fig. 2. Situation of geochemical groups of alluvial deposits within studied fragment of vertical profile, I – VI – geochemical groups

surface, 1.89 m b.l.s. and 1.92 m b.l.s. (Fig. 2). It is featured with increased concentrations of Ca (mean concentration: 9.6 mg·g^{-1}, Tab. 1) and chemical elements joined with clay grain-size fraction and sorption complex of wastes (Mg with mean concentration 1.37 mg·g^{-1} and K with mean concentration 222.71 µg·g^{-1}, Tab. 1). Comparatively high contents of these elements are probably the result of the presence of fine sand inserts within peat deposits. Similar situation can be observed in the case of group I. However, group II is characterized by high contents of Zn (maximum concentration: 24.3 $\mu g \cdot g^{-1}$) and Cu (maximum concentration: 3.77 $\mu g \cdot g^{-1}$), which are the result of strongly reductive environment within peat deposits, with presence of sulphuretted hydrogen. Such conditions accompanied the accumulation process of organic deposits within inundated fragment of floodplain or in a lateral channel, which was formed during the period of high water levels [11]. It can be seen that mean concentrations of Zn and Cu in group II (Tab. 1) are distinctly higher than in group I.

III – geochemical group of peat deposits with inserts of fine sands, featured with increased concentrations of K and low contents of Fe, Mn, Ca and Mg (Fig. 1)

Group III is represented by the sediments at the depths of 1.77–1.87 m below land surface, 1.90–1.91, 1.93 and 2.01–2.02 m b.l.s. (Fig. 2). It is characterized by high concentrations of K, which reach maximally 200 $\mu g \cdot g^{-1}$. K indicates close connection with clay grain-size fraction content. Increased concentrations of K are probably the result of increased amount of mineral admixtures in peats. Fe and Mn have low concentrations within this group (Tab. 1). These chemical elements are subjected to active migration in reductive conditions without the presence of sulphuretted hydrogen. Zn content is also low, because this element migrates easily in acid environment (also without the presence of sulphuretted hydrogen).

IV – geochemical group of peat deposits with high concentrations of Cu and Mn (Fig. 1)

The discussed group of alluvial sediments is situated at the depths of 2.17–2.23 m below land surface and 1.73, 1.76, 1.88, 2.03 m b.l.s. (Fig. 2). The group is joined only with peats and with strongly reductive environment (high Cu concentrations – maximum 9.19 $\mu g \cdot g^{-1}$ and Mn concentrations – maximum 0.717 $mg \cdot g^{-1}$). Other chemical elements are featured with relatively low contents in this group (Fig. 1, Tab. 1). Sediments of group IV were formed in the way similar to group II. Two separate groups were distinguished because of rapid increase of Mn (2.17 m b.l.s.) and Cu concentrations (1.73 and 1.76 m b.l.s.) in group IV.

V – geochemical group of peats with inserts of fine sands, characterized by high concentrations of Fe, Mn, Ca and Mg (Fig. 1)

The deposits, which belong to group V, are situated at the depth of 2.13–2.16 m below land surface (Fig. 2). Increased concentrations of Mn (mean concentration: 0.234 $mg \cdot g^{-1}$, Tab. 1) and Ca (mean concentration: 5.05 $mg \cdot g^{-1}$, Tab. 1) were noted in this group. Increased content of Mn could be the effect of reductive conditions in peat sediments. It should be noted that mean Mn concentration (0.234 $mg \cdot g^{-1}$, Tab. 1) is higher than in group IV. Besides, rapid increase of concentrations of Mn is not observed in this group. High contents of Ca are joined with inserts of fine sands in peats. Similar situation occurred in group II. However, mean Ca concentration is almost two times higher in group II than in group V (Tab. 1).

VI – geochemical group of silt and peat deposits with high concentrations of Fe, Mn, Ca, Mg and Zn (Fig. 1)

The discussed group is situated in the top part of the profile consisting of peats and sandy silts, which were deposited through vertical accretion in the area of floodplain during floods. The maximum concentrations of Fe (61.5 $mg \cdot g^{-1}$), Mn (3.356 $mg \cdot g^{-1}$) and Ca

(10.88 $mg \cdot g^{-1}$) occur in silt deposits and are the result of precipitation of these metals in the form of colloidal suspensions. Increased amounts of Fe (12.56 $mg \cdot g^{-1}$) are also present within peat deposits in this group (Fig. 2). Here, they are caused by reductive conditions with the presence of sulphuretted hydrogen. It can be seen that rapid increase of Fe, Mn, Mg and Zn concentrations shows a distinct border between flood sediments and organic deposits, which mark the place, where the Obra river bed was active in the past.

CONCLUSIONS

Distinguished geochemical groups of alluvial sediments show the following environment types:

- reductive environment within peat deposits (high concentrations of Fe, Mn, Cu and Zn) observed in the deposits, which belong to geochemical groups II, IV and V. Organic deposits within these groups were accumulated on inundated fragment of floodplain or in a lateral, stagnant water channel, which was formed during period of high water stages;
- flood deposits environment with high concentrations of Ca, Mg and K modified by migration of these elements in groundwater. The environment is represented by thin layers of fine sands within peat deposits (geochemical group I, II and V). Sandy sediments were accumulated during intensive floods. However, it should be noted that the connection between thin inserts of fine sands and changes of studied elements concentration is not precise enough to distinguish geochemical group, which would contain only thin layers of fine sands in the profile;
- flood deposits environment with high contents of Fe, Mn, Ca, Mg and Zn (top part of group VI). Silt deposits, which belong to this group, were accumulated through vertical accretion. The process of chemical elements precipitation in the form of colloidal suspensions played very important role here;
- river bed environment (fine sands of meander point bar in the bottom part of the profile) with increased concentrations of Ca, Mg and K (geochemical group I). The sediments, which belong to this group, were deposited during accumulation process on the convex bank of the Obra river bed (point bar deposition) during period of low water levels.

The conclusions presented above should be treated initially and not fully solving the problem of changes of chemical elements concentrations in alluvial sediments as indicators of particular type of depositional environment. In this study, only a fragment of vertical profile was investigated. It should be noted that the obtained results include some disturbances caused by changes of chemical constitution, which take place within alluvial deposits. The reason could be migration of chemical elements in groundwater environment, especially in mineral deposits characterized by relatively high filtration coefficient.

Acknowledgements

Research presented in this paper is a part of research program "Intensity of bed-load transport in lowland river bed: the example of the lower course of the Obra River" supported by State Committee for Scientific Research grant no P04/1215.

REFERENCES

[1] Ahmed B.Y.M.: *Climatic classification of Saudi Arabia: an application of factor-cluster analysis*, GeoJournal, **41**(1), 69–84 (1997).

[2] Busoni E., S.P. Sanchis, C. Calzolari, A. Romagnoli: *Mass movement and erosion hazard patterns by multivariate analysis of landscape integrated data: the Upper Orcia River Valley (Siena, Italy) case*, Catena, **25**, 169–185 (1995).

[3] Gerstengarbe F.-W., P.C. Werner, K. Fraedrich: *Applying non-hierarchical cluster analysis algorithms to climate classification: some problems and their solution*, Theoretical and Applied Climatology, **64**, 143–150 (1999).

[4] Lesnau A.: *Metody klasteryzacji hierarchicznej SAHN*, www.phys.uni.torun.pl/~norbert/SemMagInf/Lesnau.pdf, 2005.

[5] Mangiamelli P., S.K. Chen, D. West: *A comparison of SOM neural network and hierarchical clustering methods*, European Journal of Operational Research, **93**, 402–417 (1996).

[6] Perelman A.J.: *Geochemia krajobrazu*, PWN, Warszawa 1971.

[7] Reznickova M.: *Variability of the Molinion meadows in Slovakia*, Biologia, Section Botany, **62/6**, Bratislava 2007, pp. 675–683.

[8] Schoorl J.M., B.C. Fayos, R.J. de Meijer, J.R. van der Graaf, A. Veldkamp: *The ^{137}Cs technique applied to steep Mediterranean slopes (Part I): The effects of lithology, slope morphology and land use*, Catena, **57**, 15–34 (2004).

[9] Schwartz M., S.M.C. Payne, J.D. Restuccia, S.A. Arlene: *Does it matter how small geographic areas are constructed? Ward's algorithm versus the Plurality Rule*, Health Services and Outcomes Research Methodology, **2**, 5–18 (2001).

[10] Semmar N., B. Brugerolle, S. Boullu-Ciocca, N. Simon: *Cluster analysis: an alternative method for covariate selection in population pharmacokinetic modeling*, Journal of Pharmacokinetics and Pharmacodynamics, **32**(3-4), 333–358 (2005).

[11] Słowik M.: *Procesy kształtujące koryto rzeczne na przykładzie dolnego odcinka Obry*, Wydawnictwo Naukowe UAM, Seria Geografia, nr 76, Poznań 2007.

[12] Słowik M., T. Sobczyński, Z. Młynarczyk: *Changes of Chosen Chemical Elements Concentration in Alluvial Sediments: An Example of the Lower Course of the Obra River (Western Poland)*, Archives of Environmental Protection, **35**(1), 75–86 (2009).

[13] Statsoft: *Statistica Help: help files in Polish language version*, www.statsoft.pl 2004.

[14] Wang H., Y. Liu: *Variable cluster analysis method for building neural network model*, J. Cent South. Univ. Technol., **11** (2), 220–224 (2004).

[15] Winters J.C., K.H. Groenier, J.S. Sobel, H.H. Arendzen, M.B. de Jongh: *Classification of shoulder complaints in general practice by means of cluster analysis*, Arch. Phys. Med. Rehabil., **78**, 1369–1374 (1997).

[16] Young F.J., R.D. Hammer: *Defining geographic soil bodies by landscape position, soil taxonomy and cluster analysis*, Soil Science Society American Journal, **64**, 989–998 (2000).

Received: May 28, 2008; accepted: January 8, 2009.

GRUPY GEOCHEMICZNE OSADÓW ALUWIALNYCH DOLNEGO ODCINKA DOLINY OBRY: PRZYKŁAD ZASTOSOWANIA ANALIZY SKUPIEŃ

W dolnym odcinku rzeki Obry przeprowadzono badania nad zmianami koncentracji pierwiastków chemicznych w osadach aluwialnych. Analizy zawartości żelaza, manganu, miedzi, cynku, wapnia, magnezu i potasu przeprowadzono we fragmencie profilu pionowego cechującego się zróżnicowaną budową litologiczną. Na podstawie analiz statystycznych (analiza skupień) podjęto próbę wydzielenia grup geochemicznych osadów aluwialnego wypełnienia dna doliny Obry. Wydzielono sześć grup geochemicznych osadów reprezentujących środowisko redukcyjne w obrębie osadów torfowych, środowisko pozakorytowe (warstwy piasków drobnoziarnistych w torfach oraz mułki piaszczyste w stropie profilu) oraz środowisko korytowe (piaski drobnoziarniste w spągu profilu). Z przeprowadzonych badań wynika, że rozróżnienie wyżej wymienionych środowisk sedymentacyjnych jest możliwe również na podstawie zmian składu chemicznego osadów aluwialnych.