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MOBILITY OF CHROMIUM AND LEAD ORIGINATING FROM WEAVING INDUSTRY: IMPLICATIONS FOR RELATIVE DATING OF LOWLAND RIVER FLOODPLAIN DEPOSITS (THE OBRA RIVER, POLAND)

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Abstract: Laboratory and field experiments have been conducted to study mobility of chromium and lead in floodplain sediments. The main goal of the research was to verify a hypothesis whether changes of chromium and lead concentration could be used to estimate the relative age of floodplain deposits. The basis for undertaking such research was the presence of weaving industry centers in the Obra River valley between the 16th and the 19th century and using Cr and Pb compounds in paint recipes. The Cr and Pb contents were also analyzed in three vertical profiles unaffected by the field experiments. The age of organic sediments in each of the profiles was determined using the radiocarbon analysis. The results of the laboratory experiments have shown that the highest contents of the elements were noted in the surface layer of the sediments placed in the column. However, the contents decreased during the last phase of the experiments and both vertical and horizontal migration of both elements was observed. A more intensive mobility was observed in the field test. Its cause could be the changes of the groundwater level, floodplain inundation and pH conditions in alluvial deposits. Such processes may have influenced migration of the compounds originating from the weaving industry production; Cr and Pb contents detected in the profiles unaffected by the field experiment were too small to be used for relative dating of alluvial deposits. Moreover, the alluvial deposits with increased contents of the studied elements may be older than the period of the weaving industry development. Cr and Pb mobility was especially intensive in the profiles situated within the near bed zone of the floodplain due to regular inundation, and the activity of erosion and accumulation processes entraining the studied elements back to transport in the river bed.

INTRODUCTION

Estimation of vertical accretion rate of floodplain deposits is an important research problem. Attempts have been made to determine it using changes of the concentrations of chemical elements in a vertical profile. The main question is whether any geochemical component can be used as the indicator of the relative age of alluvial deposits. The problem is especially interesting in the case of river valleys where heavy metal sources were active in a certain period. The lower course of the Obra River and the town of Międzyrzecz (western Poland) are one of such examples (Fig. 1). The weaving industry developed in Międzyrzecz between the 16th and 19th century [18]. Textiles were also dyed during the production process which resulted in washing out the chemical elements used in paints to the river bed and their accumulation in floodplain sediments.

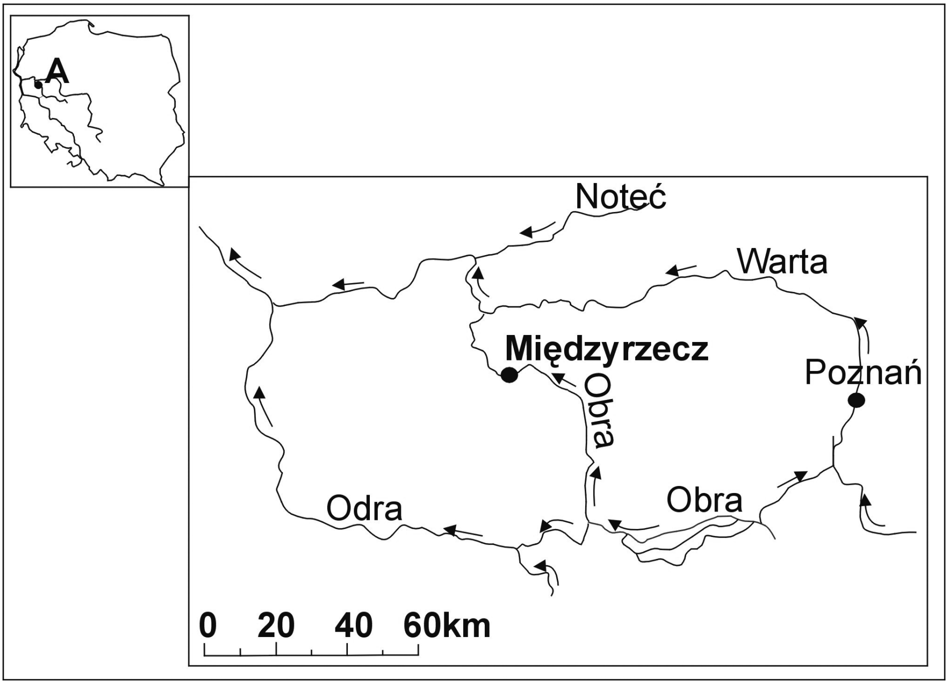


Fig.1. The Obra river in its middle and lower course . **A** – Międzyrzecz.

The chemical composition of paints used at that time was determined by a chemical analysis of a piece of dyed textile originating from the end of the 18th century. The material was offered by The Museum of Międzyrzecz. The main components of paints were chromium and lead [24]. Moreover, compounds containing Cr (III) (alum: KCr $(SO_4)_2$ $12H_2O$) and Pb (lead acetate: $Pb(C_2H_3O_2)_4$) were present in the recipes for isolation masses (Vydra 1951 in: [28, 18]) and paints [35].

The reason for choosing chromium as the potential indicator of the sediment's relative age was its low migration ability. In groundwater environment, Cr can appear in a trivalent form which is hardly soluble, and in a hexavalent form which is easily soluble and much more mobile (Robertson 1975 in: [1]; Rai & Zachara 1984 in: [16]). Cr is a geochemical component of anthropogenic origin; its high concentrations occur in sewages from tanneries and dye-houses. Lead also has a low ability to migrate in the groundwater environment. Compounds of Pb are hardly soluble when influenced by weathering processes [30]. Pb of anthropogenic origin is often accumulated within the organic and illuvial layer of soils [30]. The low migration ability of Pb was confirmed by experiments conducted by Norrström [26]. Moreover, Klink *et al.* [17] have shown that Pb was one of the least mobile elements accumulated in plants in the litoral zone of Wielkie Lake.

On the basis of the facts presented above, a hypothesis has been proposed that the changes of Cr and Pb contents in alluvial sediments reflect the period of the weaving industry development in Międzyrzecz. The main research problem was to determine whether Cr and Pb can be used as indicators of vertical accretion of floodplain deposits. The following research was performed.

Two laboratory experiments of vertical Cr and Pb migration were conducted. The first one was done in a column filled with alluvial deposits reflecting the natural sequence of deposits in the Obra valley floor. The other test was done in a column filled with alluvial fine sands. Moreover, a laboratory experiment of horizontal migration of the studied elements was done to analyze whether such mobility can influence a relative dating of alluvial deposits. There are many examples of laboratory tests determining the migration abilities of chemical elements. However, they are different from the study presented here:

- for the most part, they regard deposits other than alluvial ones (post-mining deposits: [21, 32, 8, 25] and soils: [19, 7, 26, 2];
- they refer to the migration of chemical elements only within the surface layer of deposits [11] or such migration regards only 30–40 cm thick sediment [26] without considering vertical migration to deeper parts of the sediment profile;
- in the case of alluvial sediments, they refer to the palaeomeander [20] and river bed deposits [11];
- they do not regard the problem of using chemical elements as the indicators of relative dating of sediments.

The field experiment involved the addition of Cr and Pb compounds to the floodplain deposits. It was conducted to verify the results of the laboratory tests. The studies by Simms *et al.* [32], Brown and Glynn [6], Birkefeld *et al.* [5] and Ganor *et al.* [13] have indicated significant differences between both laboratory and field experiments. Such comparison was also needed here because the migration of Cr and Pb is dependent on numerous factors such as pH [15, 9, 14] and the content of organic matter [15, 4], which can be involved in redox reactions and in this way can influence the mobility of Cr [2]. Organic matter and pH conditions play an important role in the mobility of Cr owing to reducing Cr (VI) to Cr (III) [27, 2]. Organically bound Cr (III) may also preferentially sorb to and desorb from organic portions of suspended particulates [12].

Another research task was the analysis of Cr and Pb concentration in vertical profiles unaffected by the field experiment and determining the age of organic deposits in the profiles. The analysis was done to verify whether the increased Cr and Pb contents are present in the sediments accumulated during the period of textiles production in Międzyrzecz. It should be noted that at present there are no industrial centers in the vicinity of the Obra River valley. Therefore, it is likely that the increased contents of Cr and Pb would be the result of weaving industry production and are not influenced by contemporary pollution.

RESEARCH METHODS

Laboratory experiments

The experiment of vertical Cr and Pb migration was done in a 40 x 20 x 200 cm column filled with alluvial deposits (Pic. 1A). The deposits (Pic. 1A) reflected the natural sequence of sediments in the vertical profile which was investigated in earlier studies [24]. The sediments were collected from the Obra River valley. Concentrations of Cr and Pb in the collected deposits ranged from 2 to 4 mg kg^{-1} in fine sands, respectively, and from 8 to 10 mg kg^{-1} in peats, respectively. A fuller account of chemical characteristics of the Obra

River alluvial deposits was given in Słowik *et al.* [34]. To maximize the homogeneity of the deposits, packing was performed incrementally in maximum 5 cm layers. The parameters describing the physical properties of the studied sediments were presented in Tab.1.

Tab.1. Physical parameters describing the deposits placed in the column. MD – mean diameter, SD – standard deviation

Sediment type	Fine sands with organic matter	Fine sands	Peats
Particle density (g/cm3)	1.13	1.22	0.98
Natural water content (%)	113	103	142
pH	6.6	6.0	6.5
Grain size distribution (%):			
clay fraction (< 0.002mm)	0.8	0	3.8
silt fraction (0.002-0.063mm)	6.4	5.6	22
sand fraction (0.063-2mm)	92.9	94.4	74.2
gravel fraction (> 2mm)	0	0	0
MD (phi)	2.30	2.07	3.15
SD	1.40	1.27	2.53

The column was equipped with piezometers and syringes to observe the water level and to collect water samples (Pic. 1A). Sediment samples were collected through holes in the right side of the device (Pic. 1A) every 5–10 cm of the depth of the column. In all stages of the test, water samples were also collected from a tap in the bottom of the device (Pic. 1A) to determine Cr and Pb contents.

The deposits placed in the column were supplied with alum ($KCr\ (SO_4)_2\ 12H_2O$)) and lead acetate $Pb(C_2H_3O_2)_4$). Concentrations of the compounds (alum: 54 mg dm^{-3}; lead acetate: 130 mg dm^{-3}), which were used in all laboratory and field tests, were calculated on the basis of information about weight proportions of the compounds taken from paint recipes [18], annual production of textiles in Międzyrzecz in the 16th century [18] and mean annual discharge of the Obra River (4 m^3 s^{-1}). Moreover, 1m^2 of linen textile was "bathed" in 5% solution of alum and lead acetate. Then it was rinsed in 10 dm^3 of water. Next, concentrations of Cr and Pb were determined in the water after rinsing. Approximately, the calculated concentrations reflect the daily supply of the compounds to the Obra River bed during the period of textiles production in Międzyrzecz. They were increased 10 times to achieve concentrations high enough to be measured during the experiments.

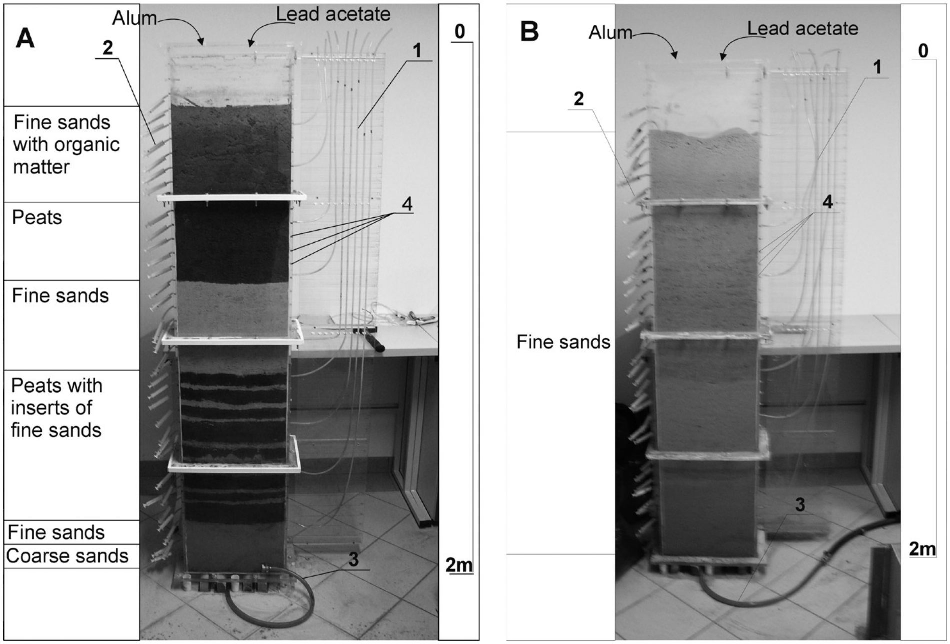
There were four stages of the experiment:

Stage I: The deposits in the column were soaked with distilled water until its level was 15 cm over the deposits' surface. Then water samples were collected. Next, the water was let out of the column. This phase was a simulation of the period which preceded the production of textiles in Międzyrzecz (when alluvial sediments were not supplied with Cr and Pb compounds). The analyses of water samples taken during this stage provided additional information about the contents of Cr and Pb before supplying the column with the compounds.

Stage II: The lower half of the column was filled with water again and the upper part was filled with the compounds of chromium and lead. Next, water samples were collected. This stage simulated the period of textile production in Międzyrzecz (supplying the Obra River valley deposits with Cr and Pb compounds).

Stage III: About 20 dm^3 of the solution was let out to initiate vertical migration of the compounds inside the column. Next, sediment and water samples were collected.

Stage IV: About 60 dm^3 of distilled water was let to pass through the deposits placed in the column. Next, sediment samples were collected. Phase IV simulated the period after the production of textiles when supplying the floodplain with the compounds was stopped.



Pic.1. The column filled with various sorts of alluvial deposits (A) and with alluvial fine sands (B).
1 – piezometers, 2 – syringes for collecting water samples, 3 – a tap for letting the water out, 4 – holes in the right side of the column for collecting sediment samples

The total duration time of the experiment was about 210 days. During each stage the collection of water and sediment samples took place 30 days after soaking the column to let the water and the compounds be mixed in static phase. The particular stages of the test were separated by 30-day-long periods, when no water or compounds were added to the column. This was a simulation of the conditions when the Obra River floodplain was not inundated. The column was flooded from top to bottom. It took minimum 50 hours to soak the deposits.

A similar experiment was performed in the column filled with alluvial fine sands (Pic. 1B) to eliminate the influence of organic matter on Cr and Pb mobility. The experimental procedure was the same as presented above.

The laboratory experiment of horizontal Cr and Pb migration was done in a 310 x 30 x 40cm column filled with fine sands and peats (Pic. 2) which reflected the Obra River alluvial deposits' sequence in the near bed zone. A part of the column was separated (Pic. 2) using a plastic plate with drilled holes secured with a filtration mesh. The separated part of the device simulated the river bed during the period of production and dyeing textiles, and was supplied with Cr and Pb compounds. The studied elements migrated to alluvial deposits placed in the remaining part of the column.

Pic. 2. Horizontal column filled with alluvial deposits. 1 – separated part of the device supplied with Cr and Pb compounds, 2 – artificial slope simulating slope of floodplain, 3 – peats , 4 – alluvial fine sands, 5 – places of samples' collection

There were 3 stages of the experiment. During each stage alum and lead acetate were added to the separated part of the device until the deposits in the column were soaked with the compounds. Sediment samples were collected in 1-meter-long sections 30 days after soaking the device, which simulated inundation of the Obra River floodplain. The samples were taken from the surface layer, the bottom layer and 15 cm depth (Pic. 2). They were collected from fine sands and peats situated at the deposits' surface layer and at 15 cm depth of the horizontal column (Pic. 2) to compare the contents of the studied elements in the two sorts of deposits. The stages of the test were separated by dry periods (each 30 days long) to simulate conditions of low water stages in the Obra River bed.

Field experiment

The experiment was conducted in the lower course of the Obra River 3 km downstream of the town of Międzyrzecz (Fig. 1), on three sites (Fig. 2) with different geologic structures (Figs. 7, 8, and 9).

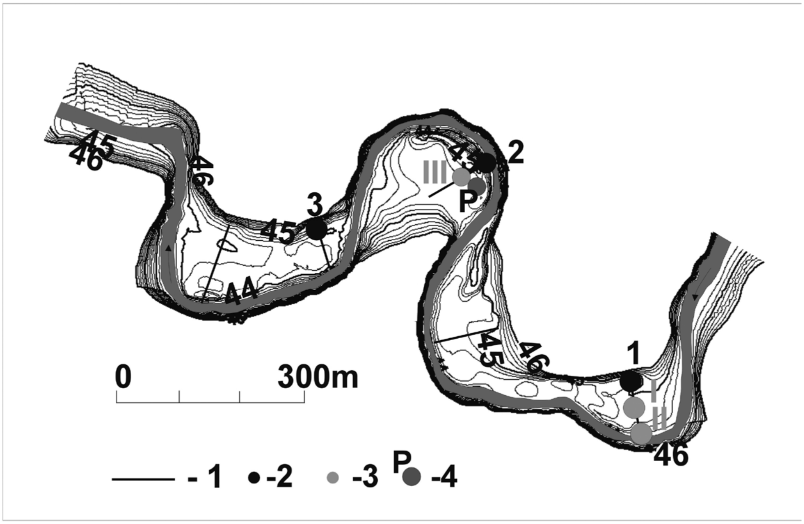


Fig. 2. Research area. 1 – geologic cross-sections, 2 – field experiment sites, 3 – sites of collection of vertical profiles unaffected by field experiment. 4 – location of piezometer

The sites' location was chosen on the basis of the study done by Słowik [33] regarding the geologic structure of alluvial deposits. On each site six PVC pipes, each 1m long, were placed in the floodplain. They were inserted in the floodplain so that they were filled with sediments. Once a month, between October 18th 2007 and September 4th 2008, they were refilled with 2.5dm^3 of compounds containing trivalent Cr (alum: KCr $(SO_4)_2$ $12H_2O$ – 2 pipes), hexavalent Cr (potassium dichromate: $K_2Cr_2O_7$ – 2 pipes) and lead (lead acetate: $Pb(C_2H_3O_2)_4$ – 2 pipes) (Fig. 3). During the experiment, monthly measurements of the groundwater level were done in a piezometer, which was installed in the vicinity of site 2 (Fig. 2).

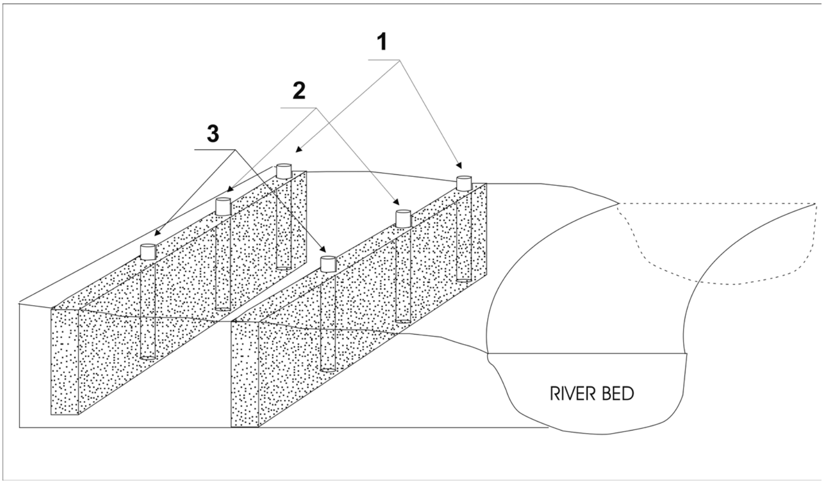


Fig. 3. Schematic of field experiment. 1 – pipes supplied with alum (Cr III), 2 – pipes supplied with lead acetate, 3 – pipes supplied with potassium dichromate (Cr VI)

Tube sample borings were done to collect vertical profiles from the pipes at the end of the experiment. Sediment samples were taken from the profiles in 10-cm-long sections for chemical analyses. It should be noted that general Cr concentration was determined in the samples without speciation of Cr (III) and Cr (VI). For that reason, the following expressions were used in the section presenting the results of the field experiment: Cr (alum) – Cr content in the profiles supplied with alum containing Cr (III), Cr (pot. dichromate) – Cr content in the profiles supplied with potassium dichromate containing Cr (VI).

Three vertical profiles unaffected by the field experiment (Fig. 2) were collected. Sediment samples were taken from the profiles in 10-cm-sections for chemical analyses. Radiocarbon age was determined in three samples taken from the bottom of organic sediments in the profiles. The purpose was to verify whether the sediments with increased contents of Cr and Pb originate from the period of textile production in Międzyrzecz. The radiocarbon analyses were done in Gliwice radiocarbon laboratory using conventional radiometric techniques (gas proportional counting, liquid scintillation counting).

In all samples collected during the laboratory and field experiments, Cr and Pb concentrations were defined using the atomic absorption spectrometry method. The measurements were done using AAnalyst 300 Perkin Elmer spectrometer (atomization in air-acetylene flame following wet mineralization and dilution of the sample in concentrated nitric acid and hydrogen peroxide).

Granulometric analyses were done for 75 samples collected during the laboratory and field work using a particle size analyzer Mastersizer 2000 to determine granulation coefficients (mean diameter and standard deviation). The coefficients were calculated using the method of moments.

RESULTS AND DISCUSSION

Laboratory experiments of vertical Cr and Pb migration

In the column filled with various sorts of deposits (Pic. 1A), high Cr and Pb contents occurred in the surface sediment layer (Cr: 549 mg kg^{-1}; Pb: 378 mg kg^{-1}; Fig.4). In the remaining part of the column, the contents of the studied elements were several times lower (Fig. 4). It was observed that greater concentrations were present in peats (5–25 mg kg^{-1}; Fig. 4) than in sand deposits (1–4 mg kg^{-1}; Fig. 4). Before starting the test the initial maximum contents of Cr reached 10 mg kg^{-1} (see section "Research methods") in peats. Organic matter and pH conditions play an important role in the mobility of Cr due to reducing Cr (VI) to Cr (III) [27, 14, 2]. The inverse process of oxidation of Cr (III) to Cr (VI) is very slow in natural systems and is possible only under high temperature and pH conditions [28, 10]. Cr (III) has very low solubility and a strong tendency to adsorb to surfaces (Sass & Rai 1987 in: 27]. However, Farmer *et al.* [12] reported that organically bound Cr (III) may also preferentially sorb to and desorb from organic portions of suspended particulates. A significant reduction of Cr content occurred in the surface layer of the sediments between the last two stages of the test (from 549 mg kg^{-1} to 297 mg kg^{-1}; Fig. 4). Chromium was flushed out from the surface layer of the deposits in the column. The contents of the studied elements in water samples collected from the column after stage I of the test ranged from 0 to 0.2 mg dm^{-3}. After the following stages Cr and Pb concentrations in water samples increased to maximum 0.6 and 2 mg dm^{-3}, respectively. Cr and Pb contents in water samples taken from a tap in the bottom of the column were lower than 2 mg dm^{-3} during all stages of the test. This fact may mean that the process of washing out Cr form the deposits was not rapid, however, it was working continuously in all the stages of the experiment. Stage IV simulated the period after the weaving industry was closed down. The observed reduction of Cr suggests that the element could have the ability to migrate down to deeper parts of the floodplain deposits, especially during periods of floods and high water stages.

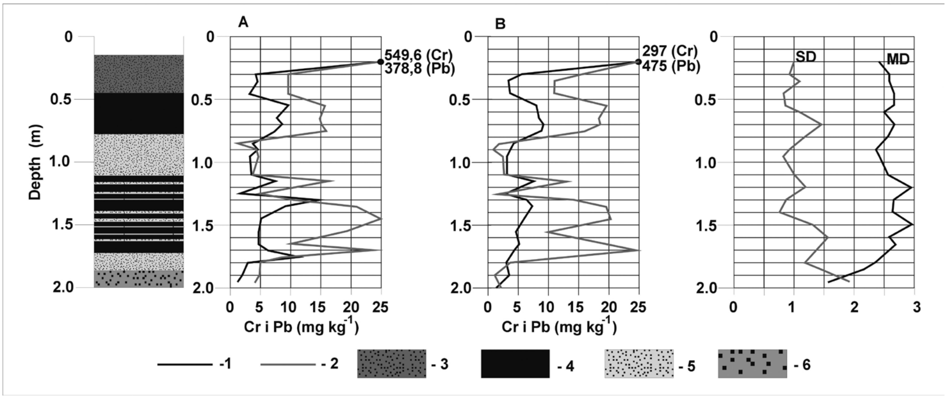


Fig. 4. Cr and Pb concentrations in the deposits placed in the column after stage III (A) and stage IV (B) of the experiment. 1 – Cr concentration, 2 – Pb concentration, 3 – fine sands with organic matter, 4 – peats, 5 – fine sands, 6 – coarse sands, MD – mean diameter, SD – standard deviation

The results of the experiment conducted in the column filled with alluvial fine sands (Pic. 1B; Fig. 5) were comparable with the presented above (Fig. 4). The highest Cr and Pb contents occurred in the surface layer of the deposits (Cr: 252 mg kg^{-1}; Pb: 699 mg kg^{-1}; Fig. 5), however, they significantly decreased after the last stage of the test. The observed decrease limits the possibility to use Cr and Pb concentrations for relative dating of alluvial deposits. In the lower parts of the column concentrations of both elements ranged from 0.4 mg kg^{-1} do 13.5 mg kg^{-1} (Fig. 5).

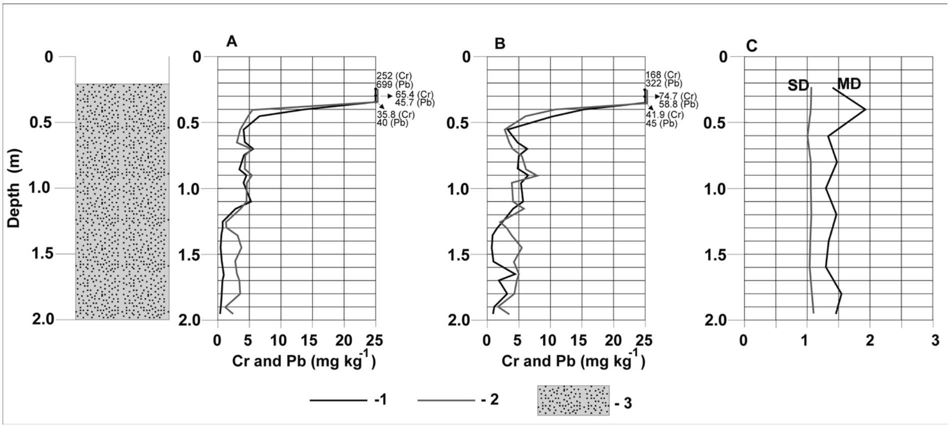


Fig. 5. Cr and Pb concentrations in alluvial fine sands placed in the column after stage III (A) and stage IV (B) of the experiment. 1 – Cr concentration, 2 – Pb concentration, 3 – fine sands, MD – mean diameter, SD – standard deviation

In water samples taken from the column filled with fine sands the Pb content reached 9.1 mg dm^{-3} and 9.2 mg dm^{-3} after stage III and stage IV of the experiment, respectively. This would point to more active migration of lead in alluvial fine sands in comparison with Cr. Maximum concentrations of chromium did not exceed 0.25 mg dm^{-3}.

Experiment of horizontal Cr and Pb migration

The results of the first stage of the experiment have shown that high Cr and Pb contents appeared in the vicinity of the separated part of the device supplied with the compounds (Fig. 6). Cr and Pb contents ranged from 223 mg kg^{-1} and 130 mg kg^{-1} in the surface layer (Fig. 6A) to 377 mg kg^{-1} and 213 mg kg^{-1} in the bottom layer, respectively (Fig. 6C). There was a distinct decrease of Cr and Pb concentration at 1m, 2 m and 3 m distance from the separated part of the device. Lead was featured with more active mobility; its concentrations were higher in comparison with Cr and reached 8.3 mg kg^{-1} at 3 m distance in the bottom layer (Fig. 6C) and 9.5 mg kg^{-1} in the surface layer (Fig. 6A). There was no significant difference in Cr and Pb contents in peats and fine sands placed in the horizontal column (Fig. 6).

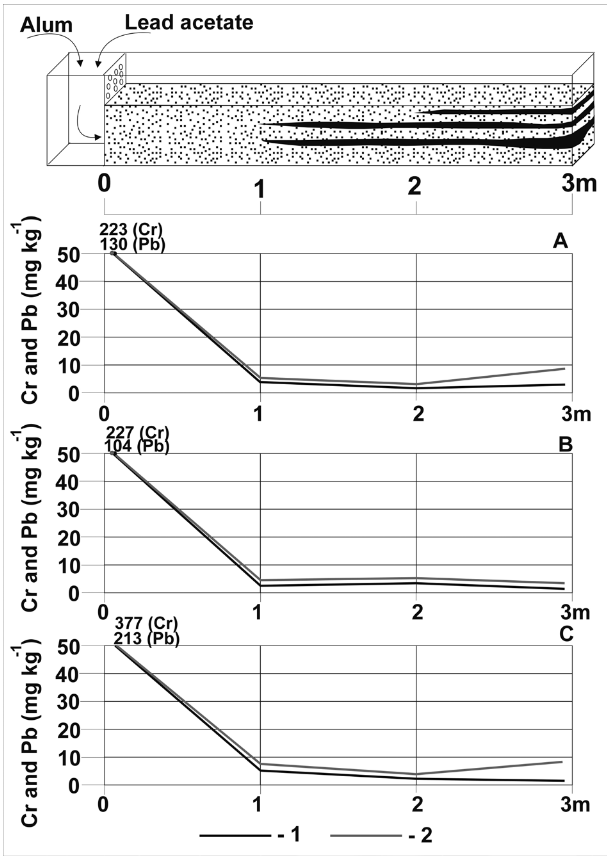


Fig. 6. Changes of Cr and Pb concentration in alluvial deposits after the first stage of horizontal migration experiment. A – Cr and Pb contents in surface layer, B – at 15cm depth, C – in bottom layer, 1 – Cr concentration, 2 – Pb concentration

The results have shown that the horizontal migration of the studied chemical elements can influence relative dating of floodplain deposits when the vertical profile of alluvial deposits is collected for chemical analyses from the near bed zone.

Field experiment

Cr (alum) (Fig. 7A, A1; 8A, A1 and 9A) was less mobile in comparison with Cr (pot. dichromate) and Pb. Its maximum contents (323 mg kg^{-1} and 474 mg kg^{-1}) were noted in the surface sediment layer – in peats and fine sands with organic matter on site 2 (Fig. 8A and 8A). Experiments done by Gong and Donahoe [15] have shown that Cr can be strongly sorbed by sandy loam soils which influences its mobility. Cr (alum) concentrations were lower in deeper parts of the profiles. However, in some cases they ranged from 80 mg kg^{-1} to 100 mg kg^{-1} (Fig. 8A1 and 9A), which indicated more active migration in comparison with laboratory tests (Fig. 4 and 5). It should be noted that Cr and Pb contents in the profiles unaffected by the field experiment presented by Młynarczyk *et al.* [24] and in this paper (Fig. 11) ranged from 5 to 15 mg kg^{-1}. This indicates that the contents of Cr and Pb presented in Figs.7, 8 and 9 come from adding the compounds to the pipes during the field test.

Cr (pot. dichromate) was subjected to more active migration (Figs. 7B, B1; 8B, B1 and 9B). On site 1 its contents were higher at 0.8 m b.l.s. (90 and 120 mg kg^{-1}) than in the surface layer (80 mg kg^{-1}) (Fig. 7B, B1 – peat deposits). Such an increment was also noted at this depth in the profiles supplied with alum (Fig. 7A, A1), however, it was much smaller. It is possible that pH conditions and the reduction process influenced the migration abilities of Cr (pot. dichromate) and that its hexavalent form was reduced to the trivalent one which is much less mobile. Bartlet and Kimble (1976 in: [31]) noted that Cr (VI) can be reduced in the presence of electron donors such as aqueous Fe (II), ferrous iron minerals, reduced sulphur compounds and soil organic matter. Gong and Donahoe [15] observed that Cr content increased when pH of solution added to the column dropped below 3.8–4.0. Baron and Palmer [3] stated that pH was a function of the solubility products of $KFe(CrO_4)_2 2H_2O$ and $KFe_3(CrO_4)_2(OH)_6$, and the activities of K^+ and $Cr_2O_7^{2-}$. Such process could have taken place in the case of the profiles on site 1 (Fig. 7B, B1). It should also be noted that the contents of Cr (pot. dichromate) ranged from 20 to 50 mg kg^{-1} in the bottom parts of the profiles on site 1 (Fig. 7B, B1). Presumably, some of the reduced chromium could form soluble organic complexes and migrate further downward the profile. This process was reported by Farmer *et al.* [12] and Shitza *et al.* [31], and could be the reason for more active migration of the studied elements in comparison with the laboratory experiments.

Lead was also subjected to active migration (Fig. 7C, C1; 8C, C1 i 9C). Its contents reached 643 mg kg^{-1} at 0.7m b.l.s. on site 2 in fine sands (Fig. 8C1) and 175 mg kg^{-1} at the same depth on site 1 (Fig. 7C1) in peats. On site 2 (Fig. 8C) Pb concentrations were higher in fine sands with organic matter (585 mg kg^{-1}) than in fine sands (239 mg kg^{-1}), so organic matter could have had some influence on Pb migration. Birkefeld *et al.* [5] observed the lowest dissolution rates of PbO in sand material. However, that was not the case in another profile on site 2 (Fig. 7C1) where its contents were higher in fine sands than in peat deposits.

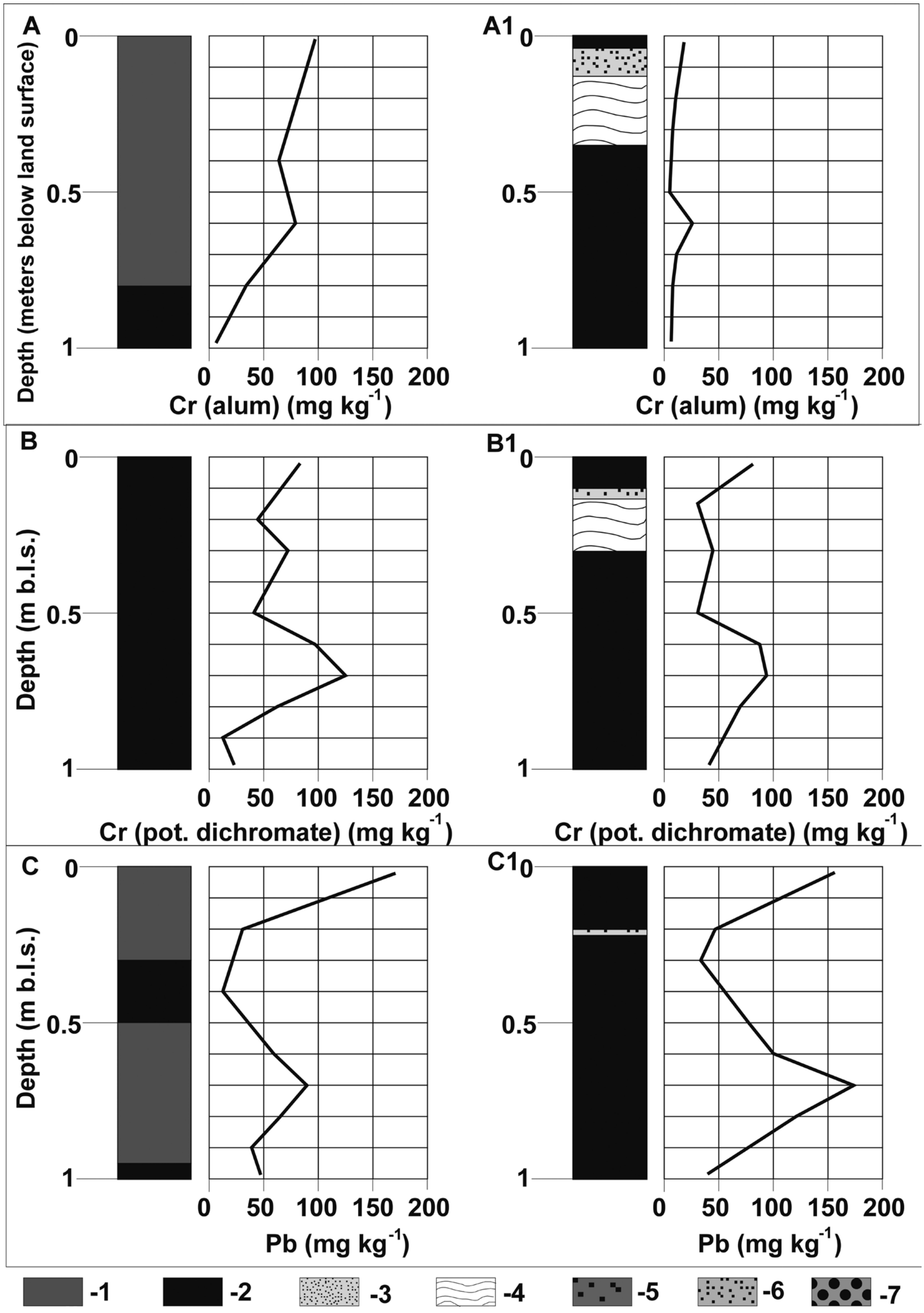


Fig. 7. Geologic structure and changes of Cr and Pb concentration in vertical profiles subjected to field experiment on site 1. A, A1 – profiles supplied with trivalent Cr compound (alum), B, B1 – profiles supplied with hexavalent Cr compound (potassium dichromate), C, C1 – profiles supplied with lead solution (lead acetate). 1 – gyttja, 2 – peat, 3 – fine sand, 4 – sandy silt, 4 – fine sand with organic matter, 6 – medium sand, 7 – coarse sand. Situation of the site – see fig. 2

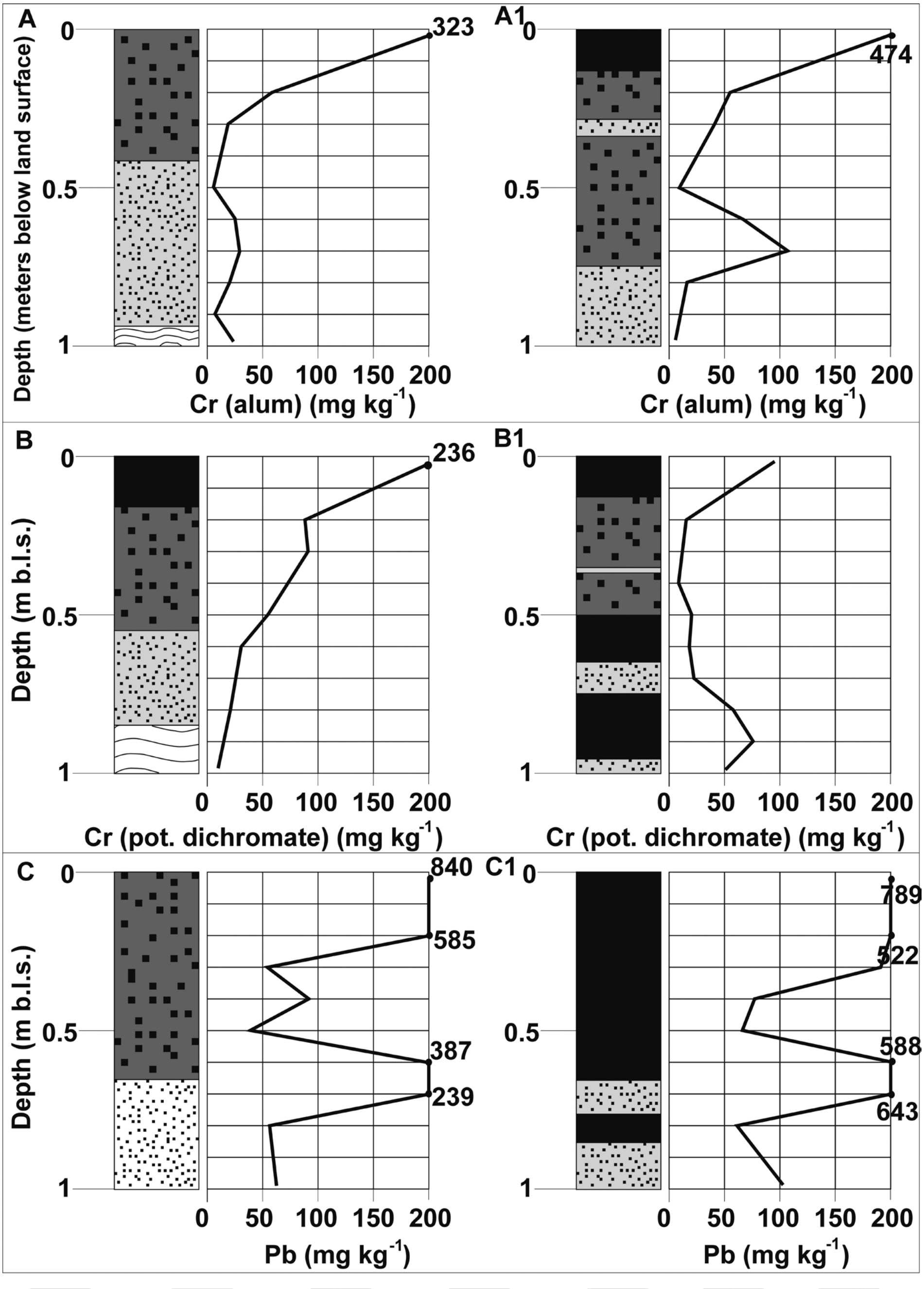


Fig. 8. Geologic structure and changes of Cr and Pb concentration in vertical profiles subjected to field experiment on site 2. Explanations – see fig.7

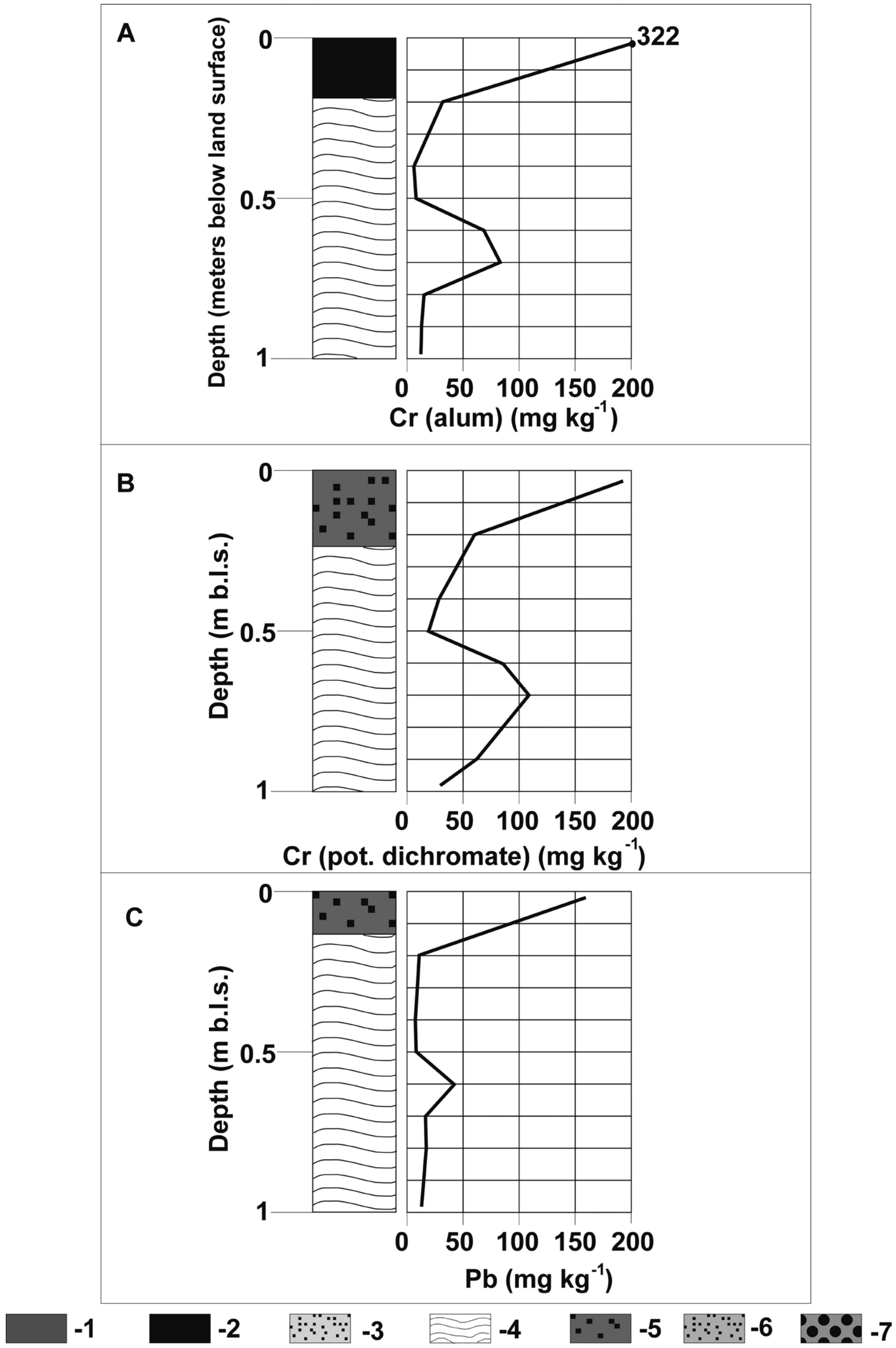


Fig. 9. Geologic structure and changes of Cr and Pb concentration in vertical profiles subjected to field experiment on site 3. Explanations – see fig.7

Significant variations of the groundwater level were observed during the field experiment (Fig. 10). During periods of high water stages (February 21st – April 15th 2008; Fig. 10) three pipes on site 2 (Fig. 8A1, B1 and C1) and all pipes on site 1 (Fig. 7) were flooded, which could influence the migration of Cr and Pb. The contents of chemical elements in alluvial deposits are influenced by its resuspention, which was reported by Calmano *et al.* (1994 in: [32]). Shitza *et al.* [31] noted that easily dissolvable Cr (VI) species became solubilized during wet periods. Another factor influencing mobility of Cr and Pb could be the oxidation degree of alluvial deposits before the flooding period [32]. Douglas & Adeney [9] have shown that concentration values of chemical elements may be altered due to the interaction between the oxic riverine flow and anoxic groundwater. Such processes could have influenced migration of the elements in the Obra River floodplain deposits. The amount of precipitation could be another important factor triggering mobility of Cr and Pb. The highest rainfall values appeared in January, April and August 2008 (Fig. 10). The annual precipitation was 648.2 mm. It should be noted that the deposits were soaked with distilled water in the laboratory experiments (Pic. 1A and B). This would suggest that chemistry and pH of rain water could have influenced greater migration of Cr and Pb in field conditions. However, no data concerning chemical properties of rain water was available.

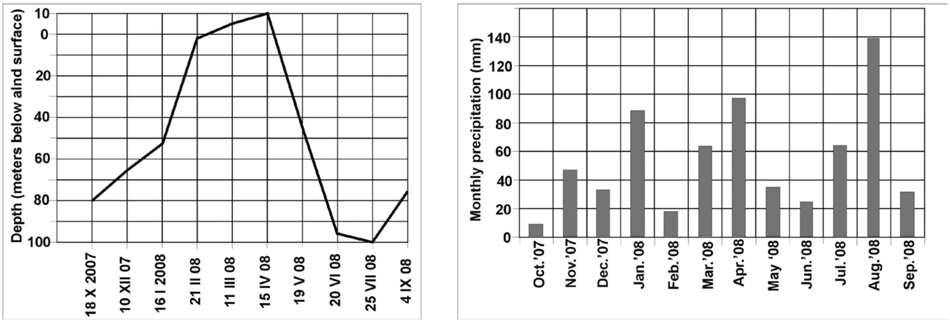


Fig.10. Groundwater levels and monthly precipitation during field experiment (rainfall data from Pszczew monitoring station 20km east of research area)

Changes of Cr and Pb concentrations in vertical profiles unaffected by field experiment

On site I (Fig. 2) increased contents of the studied elements were present in fine sands with organic matter at 0.3 m below the land surface (Fig. 11A). Such increase was also noted within peat deposits at the depth of 1.5 m and 1.9 m b. l. s. (Fig. 11A). However, the age of the bottom of organic sediments (2.0 m b.l.s.) was 1995BP ± 115 (Fig. 11A). and the deposits with increased Cr and Pb contents may be older than the period of textile production in Międzyrzecz (16th–19th century). The top part of the profile could have been influenced by erosion and accumulation processes during floods. However, such events were not as frequent as within the near bed zone. Młynarczyk and Słowik [22, 23] analyzed the changes of water stages in the Obra River bed for the period 1971–1991 and found that sites I and III were inundated only once during that time. Much less controversial was Cr and Pb distribution on site III (Fig. 11C). Increased contents of the studied elements (> 5 mg kg^{-1}) were noted at the depth of 1.4 m and 2.2 m b.l.s. (Fig. 11C). The age of the bottom of organic deposits in this profile was 950BP ± 60. It is possible that increased contents of Cr and Pb in the bottom and middle part of the profile might be the remains of the signal of textiles production in Międzyrzecz. Site III, as well as site II, was situated at a 50 m distance from the Obra River bed (Fig. 2) and was not inundated as often as the near bed zone. However, the concentrations of chemical elements should be at least an order of magnitude higher to be used as indicators of sediment age. The detected contents may be as well interpreted as natural variation of Cr and Pb in floodplain deposits. Cr contents originating from the weaving industry were influenced then by the groundwater level changes and precipitation. The original Cr contents in alluvial deposits could be altered as was shown by the results of field experiment and reported by Douglas & Adeney [9]. Pb was featured with intensive migration in the field test so its use for representing weaving industry production is impossible.

On site II (Fig. 2) the highest contents of Cr and Pb occurred at the depth of 1.9 and 2.3 m b.l.s. (Fig. 11B) but in this case it is also not possible to apply the changes to relative dating of alluvial deposits. The profile was situated in the near bed zone where erosion and accumulation processes are very frequent. Cr and Pb compounds from the weaving industry, which were accumulated within the near bed zone, were probably entrained to transport in the river bed during the next flood event. Studies regarding variations of bed-load and a suspended sediment transport rate [22, 23] have shown that the Obra River's near bed zone is inundated at least once a year between February and April. Seasonal flooding might alter the concentration of chemical elements in alluvial deposits. Douglas & Adeney [9] suggested that changes of the redox front influence geochemistry of alluvial deposits and, as a result, secondary enrichment profiles may be formed. In this way historical input of anthropogenic trace elements may be underestimated [9]. Moreover, the results of the laboratory experiment have shown that the horizontal migration of Cr and Pb can influence the results of relative dating in the near bed zone (Fig. 6).

CONCLUSIONS

Weaving industry centers were functioning in the middle course of the Obra River between the 16th and 19th century. During the production process, Cr and Pb compounds were used to dye textiles. In presented article, a hypothesis has been proposed that the compounds were being washed out to the Obra River bed and then accumulated in the floodplain deposits and that sediments' layers with increased Cr and Pb concentration may be used to determine a relative age of alluvial deposits. The laboratory experiments have shown that the contents of chemical elements were the highest in the surface layer of the deposits placed in the column. However, vertical migration of Cr and Pb was observed (Fig. 4 and 5); the contents in the surface layer significantly decreased after phase IV of the experiments simulating the period when the production of the textiles was stopped. Moreover, the horizontal migration experiment indicated that migration of Cr and Pb could influence the results of relative dating of floodplain deposits within the near bed zone.

The migration of Cr and Pb in the field experiment was more intensive in comparison with the laboratory tests. This means that there are more factors influencing the mobility of chromium and lead in the field than in laboratory conditions. One of the reasons could be pH changes, especially in the case of Cr originating from potassium dichromate. It is

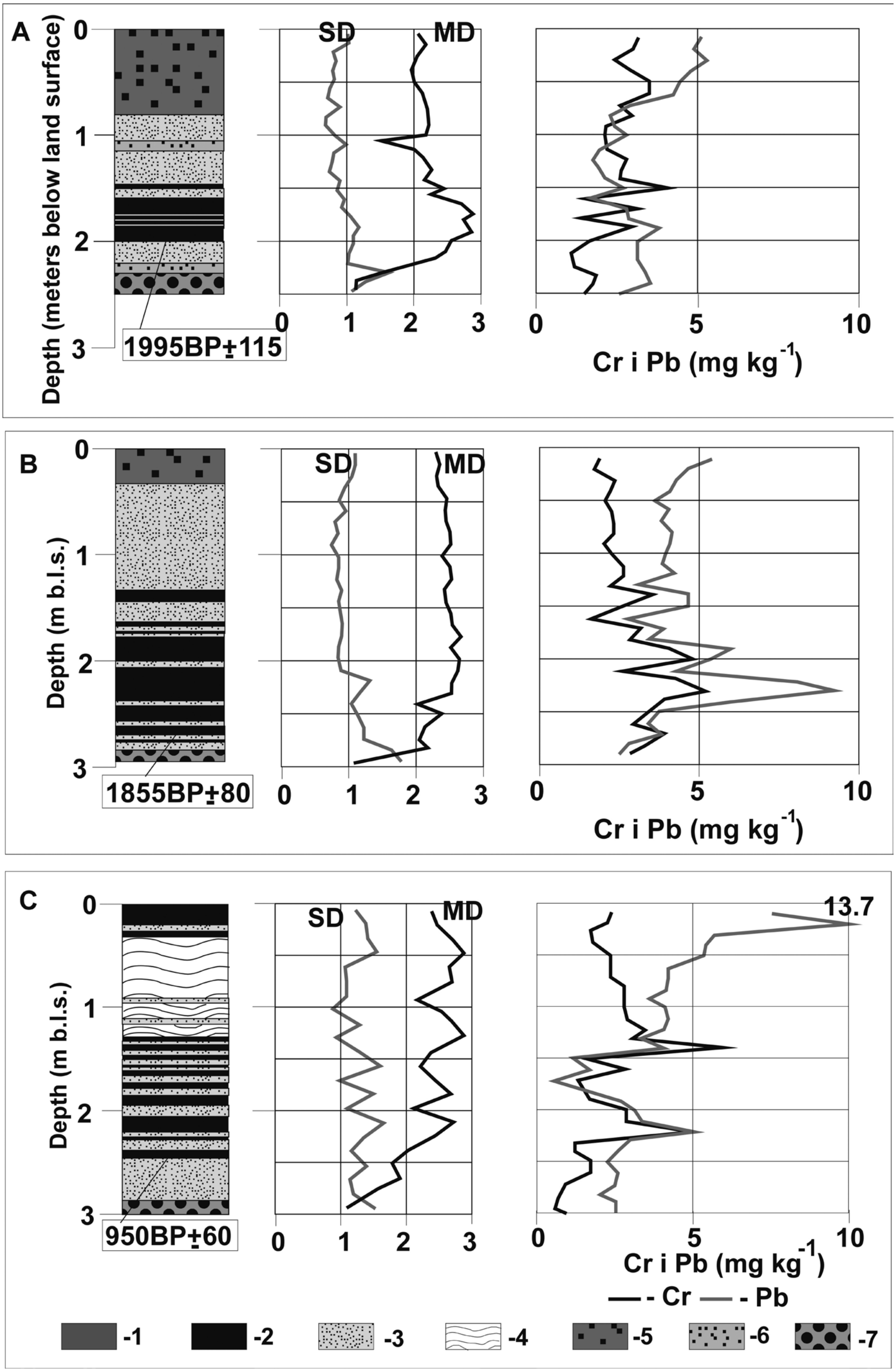


Fig.11. Geologic structure, granulation features and changes of Cr and Pb concentration in vertical profile on site I (A), site II (B) and site III (C) (unaffected by field experiment). MD – mean diameter, SD – standard deviation. Other explanations – see fig. 7

probable that the reduction process to the trivalent form of chromium took place in the profiles with organic deposits (Fig. 7). Another factor was the variability of groundwater levels and inundation of site 1 (Fig. 2 and 7) and site 2 (Fig. 2 and 8). The migration of Cr and Pb could have been influenced by dilution, especially within surface layer. Chemistry and pH of rain water could also control the migration of the studied elements. Cr (alum) was featured with relatively lower mobility in comparison with Cr (pot. dichromate) and Pb. Similarly to the laboratory tests, its highest contents were present in the surface layers of particular profiles (Figs.7–9). Possibly a complex process of adsorption and immobilization took place here.

Changes of Cr and Pb contents in vertical profiles unaffected by the field experiment have shown that it is not possible to use them for a relative dating of alluvial deposits. The increased contents of the elements appear in several places in the vertical profiles. However, the deposits may be older than the period of the textiles production in Międzyrzecz. Moreover, the concentrations would have to be at least an order of magnitude higher to be used for relative dating of alluvial deposits. The groundwater level changes and precipitation might have altered Cr and Pb contents in the profiles unaffected by the field experiment on site I and III (Fig. 11 A and C). Changes of chromium concentration within the near bed zone cannot be applied to a relative dating because its regular inundation may alter the concentration values of chemical elements in alluvial deposits. The use of Pb concentration changes in all profiles is also disputable due to its intensive migration observed in the field test.

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MIGRACJA CHROMU I OŁOWIU POCHODZĄCEGO Z PRZEMYSŁU SUKIENNICZEGO: MOŻLIWOŚCI WYKORZYSTANIA KONCENTRACJI PIERWIASTKÓW DO WZGLĘDNEGO DATOWANIA OSADÓW RÓWNINY ZALEWOWEJ (RZEKA OBRA)

Na drodze eksperymentów laboratoryjnych i terenowych przeprowadzono badania nad zdolnościami migracyjnymi chromu i ołowiu w osadach aluwialnych. Głównym celem było określenie, czy zmiany koncentracji tych pierwiastków mogą być wykorzystane do względnego datowania osadów równiny zalewowej. Podstawą do przeprowadzenia takich badań były ośrodki przemysłu sukienniczego funkcjonujące w dolinie Obry w okresie od XVI do XIX wieku oraz związki chromu i ołowiu znajdujące się w barwnikach do tkanin. Zawartość badanych pierwiastków (niezakłócona przez eksperymenty terenowe) została również określona w trzech profilach pionowych. Osady w każdym z profilów wydatowano za pomocą metody radiowęglowej. Wyniki eksperymentów laboratoryjnych wskazały, że najwyższe stężenia badanych pierwiastków wystąpiły w powierzchniowej warstwie osadów umieszczonych w kolumnie. Jednak w ostatniej fazie doświadczenia zaobserwowano spadek koncentracji chromu i ołowiu w tej warstwie, co wskazywałoby na ich migrację w osadach poddanych eksperymentom. Bardziej intensywną migrację badanych komponentów stwierdzono w eksperymentach terenowych. Jej przyczynami mogły być wahania poziomu wód gruntowych, podtapianie równiny zalewowej przez wody wezbraniowe oraz zmiany wartości pH w osadach aluwialnych. Procesy te mogły wpłynąć na migrację pierwiastków pochodzących z barwienia tkanin. Wskazują na to stężenia chromu i ołowiu w profilach niezakłóconych przez eksperymenty terenowe. Są one zbyt mało zróżnicowane, aby wykorzystać je do względnego datowania osadów aluwialnych. Ponadto osady, w których stwierdzono podwyższone zawartości badanych pierwiastków, są starsze niż okres produkcji tkanin w tym regionie. Migracja chromu i ołowiu była szczególnie intensywna w profilu usytuowanym przy brzegu koryta Obry. Przyczyną tego było regularne zalewanie tej części dna doliny oraz procesy erozji i akumulacji powodujące włączanie badanych komponentów do transportu w korycie Obry.