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STUDY OF ALUMINIUM SULPHATE COMPLEXES OF SURFACE WATER AND FRACTIONATION OF ALUMINIUM FROM BOTTOM SEDIMENT

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Abstract: The paper presents results of aluminium concentration determination in the samples of surface water and bottom sediments of the Mała Wełna River (West Poland). In the surface water the concentration of aluminium varies in the range from 4.14 to 25.9 μg/dm^3. With use of the Mineql+ program the concentration of the aluminium sulphate complexes in the water samples studied has been determined in a model way. In the bottom sediments samples of the river aluminium has been determined in the granulometric fractions of the grain sizes > 2.0; 2.0–1.0; 1.0–0.5; 0.5–0.25; 0.25–0.1; 0.1–0.063; < 0.063 mm, using the sequential extraction scheme proposed by Tessier *et al.* The lowest concentration of aluminium has been found in the granulometric fraction 0.5–0.25 mm, while the highest in the fractions 0.1–0.063 and < 0.063 mm. An elevated concentration of aluminium has been also noted in the fraction > 2.0 mm. Taking into regard the chemical fractions the lowest concentration of aluminium has been found in the exchange fraction and the fraction bounded to carbonates (fractions I and II), whereas the highest concentration of aluminium has been determined in the lithogenic fraction (fraction V). The methods of sample preparation for analysis of aluminium in bottom sediments were compared. It was observed that higher concentration of aluminium was present in grounded samples without its influence on grain size fractions. The concentration of aluminium in surface water samples has been determined by the GF-AAS, while in bottom sediments by F-AAS.

INTRODUCTION

The natural content of aluminium in the Earth's crust (7.8% of the total mass of the Earth) and susceptibility to external factors and numerous reactions occurring in natural environment is reflected in its forms of occurrence which condition its degree of bioavailability and mobility in aquatic ecosystems [7, 16, 21, 27]. The aluminium concentration in surface waters most frequently is at the range from 60 to 300 μg/dm^3, while river waters are characterized by the average aluminium concentration of 64 μg/dm^3 [17]. However, it should be emphasized that such low aluminium concentrations occur in the aquatic ecosystems with stable conditions of temperature, pH reaction, redox potential or the amount of inorganic and organic contaminants in waters. The variability of environmental conditions may affect the shift of balance in the sorption – desorption and water – sediment systems, increasing at the same time the occurrence possibility of dissolved, and as a result available, forms of aluminium. The highest solubility of aluminium occurs in the waters of strongly acid environments (for example, in the areas of frequent volcanic activity or the zones of sulfide deposits oxidation) or strongly alkaline environments (for example, in the areas of alkaline lakes, the zones of low-pressure products dissolution or the zones of thermal metamorphism of carbonate rocks). As a result, aluminium may occur at the levels exceeding the acceptable concentrations in drinking water, which is toxic for living organisms. Aluminium in aqueous solutions is characterized by amphoteric properties and may create both cation and anion complexes, organic and inorganic, with the tendency towards polymerization [32]. The factors which determine the type of the complex include pH reaction of water, temperature, concentration of ligands and ionic strength of solution [22]. Depending on the form of complex compounds, the aluminium complexes created are characterized by different toxic influence on living organisms [2, 3, 15, 23]. The inorganic monomeric aluminium with fluoride and sulphate ions complexes is considered the toxic form of aluminium [9, 10, 14]. In the environment with a high level of acidity, sulphate ions make the main anion which occurs together with dissolved inorganic forms of aluminium and creates complex with them [21]. The presence of dominating aluminium-sulphate complex forms depends on the sulphate ions concentration in the environment. The ions $AlSO_4^+$ occur with low concentrations, while the ions $Al(SO_4)_2^-$ are characteristic for higher concentrations of SO_4^{2-} [22]. The $Al\text{-}SO_4$ complexes are dominant only with the high concentrations of sulphate ions and low $pH < 4.5$ and they are not as stable as the aluminium fluoride complexes [8, 33].

The aim of the research was (1) the determination of aluminium concentration in surface waters, (2) the identification of aluminium forms in bottom sediments by means of the sequential extraction procedure, (3) the assessment of the influence of a granulometric fraction size on aluminium concentration, (4) the assessment of the influence of sample preparation on aluminium concentration at particular stages of the sequential extraction procedure, (5) modeling with the use of Mineql+ program and determination of the concentration of aluminium-sulphate complex forms in the investigated water samples.

MATERIALS AND METHODS

Study area

The Mała Wełna River catchment area lies in the centre of the Wielkopolsko-Kujawska Lowland [18]. The river is 83.8 km long and its catchment area is 688 km^2. Up to the profile Kiszkowo at the end of the catchment fragment studied, the Mała Wełna River flows through eight lakes with a total water surface area of 392.8 ha and a complex of fish ponds with a surface area of 235.1 ha (Fig. 1). The catchment area of the river is mostly agricultural (arable land 82.7%), forests (8.0%), orchards (0.3%) and idle land (9.0%). The area of the catchment fragment studied is 342 km^2, and the length of the river in this fragment is 45.3 km, with a slope of 0.58‰ [17, 18].

Sample collection and preparation

Once a month from May to August 2006, the samples of water and bottom sediments were collected at nine sites along the course of the Mała Wełna River (Fig. 1).

The water samples were collected with the Toń 2 sampler and placed into polyethylene (PE) bottles. The bottom sediment samples were collected with the Czapla-1 core-

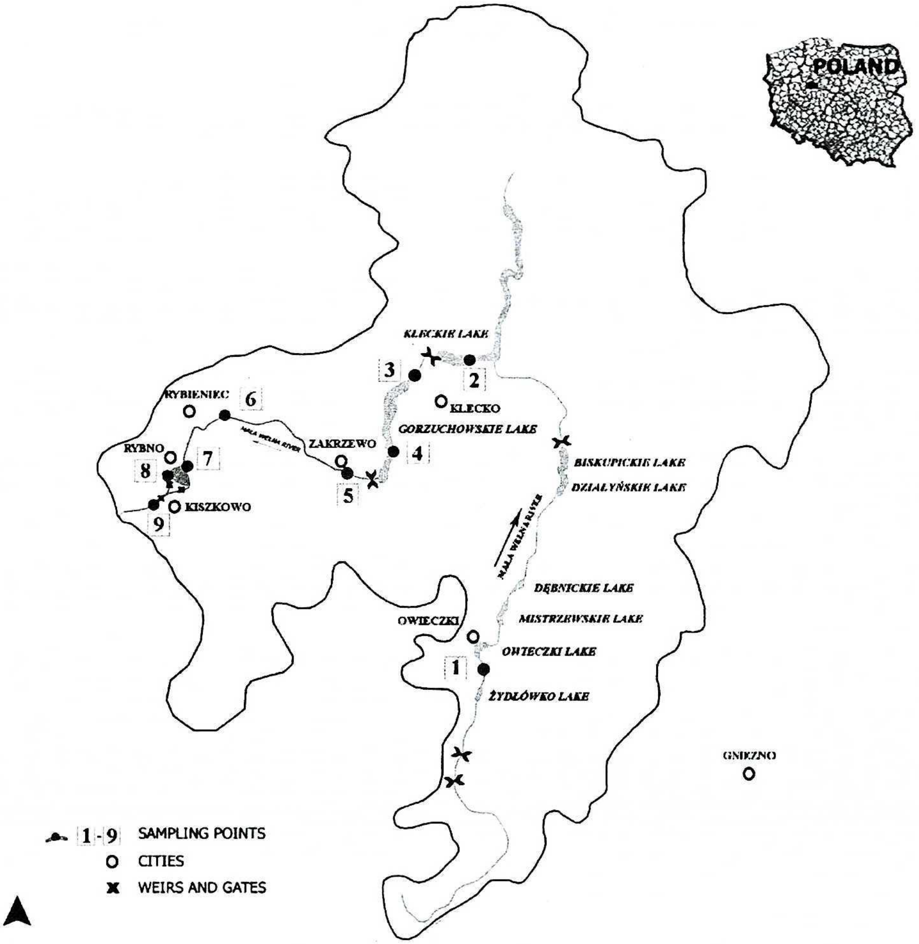

Fig. 1. Sampling points of water and bottom sediment (the Mała Wełna River)

sampler (Mera-Błonie, Gdańsk, Poland) and placed into PE containers. The sediment sample was dry sieved into seven-grain size fractions > 2.0 mm, 2.0–1.0 mm, 1.0–0.5 mm, 0.5–0.25 mm, 0.25–0.1 mm, 0.1–0.063 mm, < 0.063 mm through a LAB-11-200/UP mechanical shaker (Brzesko, Poland) with a series of stainless steel sieves. In order to differentiate and conduct quantitative determination of aluminium forms in particular granulometric fractions of bottom sediments samples, the modified sequential extraction scheme suggested by Tessier *et al.* was used (Tab. 1).

Chemical analysis

The determination of total aluminium concentration in water samples was performed by means of the graphite furnace atomic absorption spectrometry (GF-AAS). The atomic absorption spectrometer SpectrAA 20 Plus (Varian, Australia) was used for the determinations. The aluminium determinations in granulometric fractions of bottom sediments were performed with use of the absorption spectrometry with flame atomization (F-AAS) technique on the two-beam Perkin Elmer instrument, model AAnalyst 300 (Perkin Elmer,

Table 1. Operating parameters for determination of aluminium by GF-AAS and F-AAS spectrometers

		GF-AAS	F-AAS
Wavelength	[nm]	309.3	
Slit	[nm]	0.5	
Lamp current	[mA]	6	25
Flow of C_2H_2	[dm^3/min]	–	6
Flow of N_2O	[dm^3/min]	–	8,5
Flame temperature	[°C]	–	3000
Argon flow	[dm^3/min]	3.0	–
Drying	[°C]	120	–
Drying time	[s]	40	–
Ashing	[°C]	1000	–
Ashing time	[s]	2	–
Atomization	[°C]	2600	–
Atomization time	[s]	2	–
Cleaning	[°C]	2700	–
Cleaning time	[s]	2	–
Delay time	[s]	–	2
Measurement time	[s]	–	3
Number of replications	–	3	

Norwalk, Connecticut, USA). The optimized conditions for aluminium determinations have been presented in Table 2.

Concentration of SO_4^{2-} was determined by gravimetric method, pH reaction of the surface water was determined by a multifunctional measuring device, Multi 197, manufactured by WTW (Weilheim, Germany).

Table 2. Optimized conditions of sequential extraction procedure proposed by Tessier *et al.* [30] with modifications by Sobczyński *et al.* [25]

1 g of sample of bottom sediment			
Extraction steps	reagents	time [h]	temperature [°C]
I	10 cm^3 of 1 M CH_3COONH_4, pH = 7.00	1	room
II	20 cm^3 of 1 M CH_3COONa acidify to pH = 5.00 with CH_3COOH	2	room
III	20 cm^3 of 0.04 M $NH_2OH{\times}HCl$ in 25% CH_3COOH	5	95
IV	5 cm^3 of 0.02 M HNO_3 + 5 cm^3 of 30% H_2O_2, pH = 2.00	2	85
	5 cm^3 of 30% H_2O_2, pH = 2.00	3	85
	10 cm^3 of 3.2 M CH_3COONH_4 in 20% (v/v) HNO_3	0.5	room
V	3 cm$_3$ of HNO_3 + 2 cm^3 of 30% H_2O_2	0.5	95
	3 cm^3 of HF + 2 cm^3 30% H_2O_2	0.5	
	3 cm^3 of HF + 3 cm^3 HNO_3	1	

Reagents

All the reagents used were of analytical grade, and the water was deionized with a resistance > 18 MΩ in a Milli Q-RG apparatus (Millipore, France). The reference standard solutions were made of commercial standards for AAS analysis by Merck (Merck, Darmstadt, Germany).

RESULTS AND DISCUSSION

The total aluminium concentration in the all samples of surface waters of the Mała Wełna River in the research period from May to August 2006 was in the range from 4.14 to 25.9 μg/dm^3, for pH 7.1–7.5. Concentration of sulphates was in the range of 91.8–197.1 mg/dm^3. The lowest concentrations of aluminium were observed at site No. 6, whereas the highest – at the sampling site No. 7 (fish ponds) (Fig. 2). The similar aluminium concentrations as at site No. 6 were observed at sampling sites No. 2 and 4 (Kłeckie Lake and Gorzuchowskie Lake) and in Zakrzewo (site No. 5). During the analysis of variability of aluminium concentration in time, the lowest and highest concentrations were observed in May, at site No. 2 (Kłeckie Lake) and No. 7 (fish ponds) respectively. It should be stressed that the increase of aluminium concentrations was observed in the Mała Wełna River at sites No. 3 and 7 to 9 in comparison with other research points.

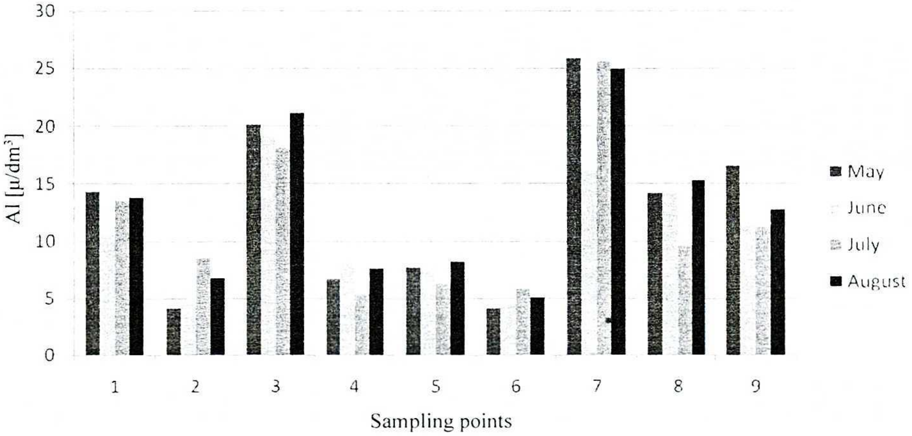

Fig. 2. Concentration of aluminium in water samples of the Mała Wełna River

Based on the obtained results it was observed that, together with the increase of [H$^+$] concentration, the total concentration of aluminium decreased. On the other hand, the decrease of the [H$^+$] was accompanied by the increase of aluminium content, which has been graphically presented in Figure 3.

The total aluminium level in the investigated water samples collected from the Mała Wełna River was low in comparison with, for example, the total aluminium content in the Vienne Royere River (from 16.4 to 100.6 μg/dm^3, pH 5.8–7.9), or in the Vienne Peyrelevade River (from 22.4 to 130.5 μg/dm^3, pH 5.7–6.8) [14]. Definitely higher concentrations of total aluminium were observed in the Vezare River (from 45.2 to 146.4 μg/dm^3,

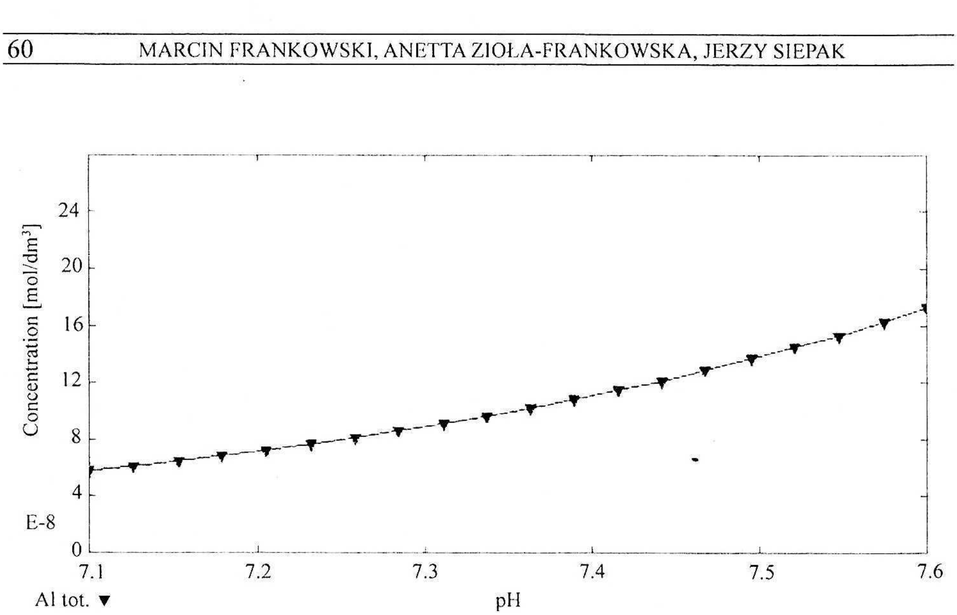

Fig. 3. Concentration of total aluminium in the function of water Ph for all analyzed samples

pH 5.6–6.8), the Grande Creuse (from 9.2 do 141.2 μg/dm^3, pH 6.5–7.4), or the Gartempe (from 8.7 do 274.8 μg/dm^3, pH 6.2–7.0) [15]. The rivers were located in the areas of high contamination level, similarly to the surface waters of Adirondack, Maine or Florida, which contained 8.1–756; 8.1–810; 8.1–1350 μg/dm^3 of total aluminium respectively [15]. The increased concentrations of aluminium from 27 to 1080 μg/dm^3 were determined in the waters exposed to acid rain in the Czech Republic, and from 81 to 1194 μg/dm^3 in the waters exposed to air pollution in northern England [20]. In the case of lack of exposure of the river waters to air pollution, the total aluminium concentration amounted to < 1.0 μg/dm^3 in Birkenes, and in the case of acid deposition, the aluminium concentration was much higher and it amounted to 110 μg/dm^3 [5]. In order to determine the content of aluminium-sulphate complex froms occurring in the waters of the Mała Wełna River, the Statisica 7.1 packet (StatSoft, Poland) and the Mineql+ program 4.5 (USA) were used. Using the Statisica 7.1 packet, the data standardization was done. The data were obtained through calculations with use of the Mineql+ 4.5 program (Tab. 3). The data after standardization are presented in Figure 4.

In the case of aluminium-sulphate complexes, it was observed that, together with the increase of [H$^+$] and sulphate ions, the concentration of $AlSO_4^+$ and $Al(SO_4)_2^-$ complexes increases, with the simultaneous decrease of the total aluminium content. The dominating complex form in the investigated samples was $AlSO_4^+$ (Fig. 5). On the other hand, the increased pH level was accompanied by the disintegration of sulphate complexes with the simultaneous aluminium release. It resulted from the fact that complexes of aluminium with sulphates are characterized by low values of stability constants, log K for $AlSO_4^+$ and $Al(SO_4)_2^-$ amounts to 3.89 and 4.92 respectively (Figs 4 and 5).

It should be emphasized that, despite determining a low concentration of total aluminium in the investigated waters, only quantitative and qualitative defining of its speciation forms, and especially the inorganic monomeric form which includes the toxic form, will enable the assessment of its actual risk level for the river ecosystem. The forms

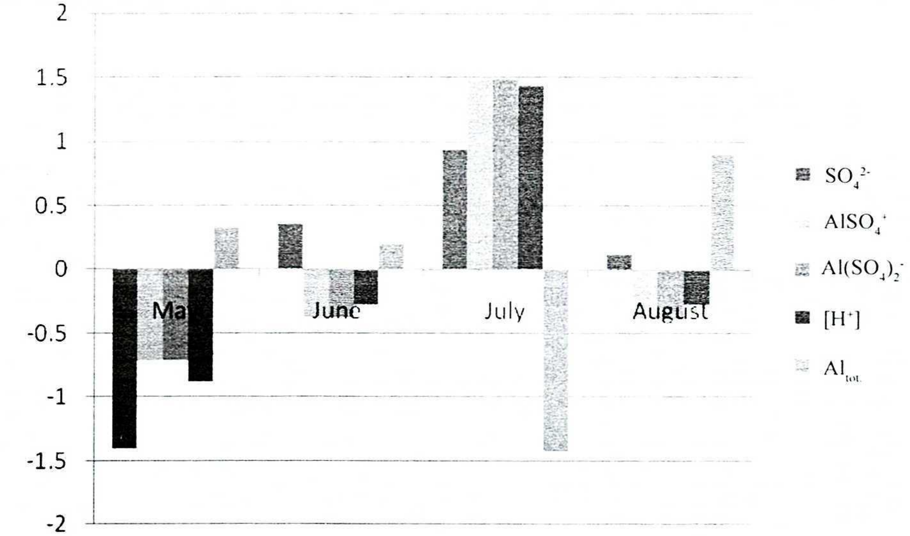

Fig. 4. Co-occurrence of SO_4^{2-}, $AlSO_4^+$, $Al(SO_4)_2^-$, total Al and amount of hydrogen ions after standardization (sampling point No. 5)

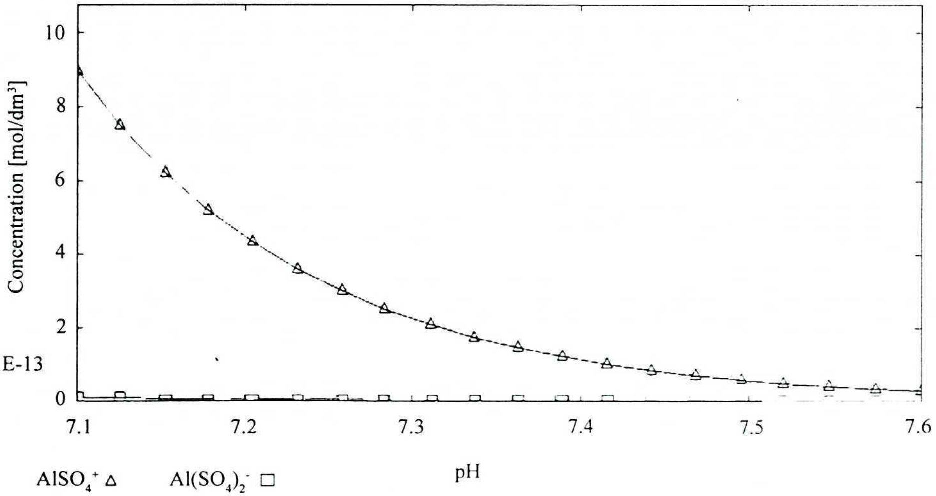

Fig. 5. Concentration of $AlSO_4^+$ and $Al(SO_4)_2^-$ complexes in the function of water pH

which create monomeric aluminium are its complex with fluorides, phosphates and sulphates [4, 31]. Aluminium-sulphate complexes occur in the form of $AlSO_4^+$ and $Al(SO_4)_2^-$ ions and their presence in river ecosystems depends on sulphate ions concentration and on the pH value. This dependence was used while studying the concentration of aluminium complexes with sulphates based on the actual results of the total aluminium concentration and the sulphates concentration by means of the Mineql+ program. The obtained results demonstrated that the dominating form in the waters under investigation was $AlSO_4^+$ (Fig. 5), and its highest contents occurred in May (Tab. 3).

Table 3. Concentration of aluminium, sulphate and [H+] in surface water of the Mała Wełna River (sampling point No. 5) and calculated concentrations of Al-SO_4 complexes from Mineql+ program

	May	June	July	August
	[mol/dm^3]			
SO_4^{2-}	1.41E-03	1.56E-03	1.61E-03	1.54E-03
$AlSO_4^+$	6.75E-14	1.50E-13	6.15E-13	1.48E-13
$Al(SO_4)_2^-$	1.02E-15	2.51E-15	1.06E-14	2.44E-15
$[H^+]$	3.16E-08	3.98E-08	6.31E-08	3.98E-08
Al_{tot}	2.85E-07	2.81E-07	2.30E-07	3.03E-07

The $Al(SO_4)_2^-$ form occurred at the lower concentration levels, due to the low concentration of sulphates in the investigated samples collected from the Mała Wełna River and the pH reaction of water (Fig. 5). Both isolated forms represent monomeric inorganic aluminium, which has toxic influence on living organisms. Similar trend like for sample No. 5 was observed for other analyzed sampling points (Tab. 4). Table 4 presents mean values of aluminium and sulphates and calculated values of aluminium sulphate complexes [mol/dm^3].

Table 4. Concentration of aluminium, sulphate and $[H^+]$ in all samples of surface water of the Mała Wełna River and calculated concentrations of Al-SO_4 complexes from Mineql+ program (May – August)

Sampling points	Al_{tot} [mol/dm^3]	SO_4^{2-} [mol/dm^3]	$[H^+]$	$AlSO_4^+$ [mol/dm^3]	$Al(SO_4)_2^-$ [mol/dm^3]
1	4.61E-07	1.74E-03	2.24E-08	7.48E-14	1.39E-15
2	2.35E-07	1.60E-03	1.58E-08	8.86E-15	1.52E-16
3	7.26E-07	1.49E-03	2.24E-08	1.01E-13	1.61E-15
4	2.48E-07	1.56E-03	1.58E-08	9.11E-15	1.52E-16
5	2.68E-07	1.51E-03	4.47E-08	5.84E-13	9.46E-15
6	1.85E-07	1.53E-03	7.08E-08	2.50E-12	4.10E-14
7	7.78E-07	1.42E-03	5.62E-08	3.96E-12	6.02E-14
8	4.61E-07	1.18E-03	5.01E-08	1.24E-12	1.56E-14
9	5.15E-07	1.18E-03	5.01E-08	1.38E-12	1.75E-14

According to Kroglund and Finstad the sum of all forms of monomeric aluminium with the concentration of 1.5 to 3.0×10^{-7} mol/dm^3 is toxic for the Atlantic salmon [19]. However, the obtained concentrations for the $AlSO_4^+$ (max. 6.15×10^{-13} mol/dm^3) and $Al(SO_4)_2^-$ (max 2.51×10^{-15} mol/dm^3) forms do not pose any danger for the living organisms studied in the Mała Wełna River. Contrary to the toxic concentrations of aluminium in the Vienne Royere River (1.1×10^{-6} mol/dm^3), or the Vienne Peyrelevade River (6.0×10^{-7} mol/dm^3) [14], higher values were suggested by Kroglund and Finstad [19]. In comparison to Kroglund and Finstad higher concentrations of the toxic aluminium form were also determined in the Vezer River (from 0.2×10^{-5} to 0.59×10^{-3} μmol/dm^3), the

Grande Creuse (from 0.27×10^{-4} to 0.544×10^{-3} μmol/dm^3), the Gartempe (from 0.6×10^{-5} to 0.112×10^{-3} μmol/dm^3) [15, 19].

The water samples analysis enabled the determination of various forms of aluminium but, in order to find out complete information of the potential cycle of this element in the studied aquatic ecosystem, it was essential to determine its mobile forms in bottom sediments. The obtained results of aluminium fractionation, in particular granulometric fractions, for bottom sediments were presented on the example of the research site No. 5 (Fig. 6) and presented trend of occurring of particular fractionation form of aluminium was observed for all samples from the study area. In the two first most toxic fractions, that is the exchangeable one and the one associated with carbonates, the concentration of aluminium in all the analyzed samples was low and it reached the maximum value of up to 5.65 mg/kg d.m. (for granulometric fraction < 0.063 mm). Higher concentrations of aluminium were determined in the chemical fraction associated with Fe-Mn oxides (fraction III).

The highest concentrations of aluminium were determined in the grain size fraction > 2.0 mm which amounted to 1720 mg/kg d.m., while for the fraction 0.25–0.1 mm the aluminium concentration amounted to 356 mg/kg d.m. It is noteworthy that the aluminium occurring in this fraction is less mobile than in the case of fractions I and II, hence its penetration to the water depth is more difficult. In the fraction connected to organic matter (fraction IV), the highest concentration of metal occurred in grain size fraction < 0.063 mm and it amounted to 1710 mg/kg d.m. Sobczyński *et al.* [25], on the example of bottom sediments of the Oder River and lake sediments, also observed the increase of aluminium concentration in this fraction. Sobczyński *et al.* related this fact to the increase of organic matter concentration in bottom sediments [25, 26]. Sin *et al.* while performing mineralization with HCl i HNO_3 acids in the samples of river sediments of the Shing Mun River, obtained the aluminium concentration at the levels from 0.249 to 114 mg/g d.m. [24]. When these values are compared with the concentrations obtained for fraction IV in the sediments of the Mała Wełna River, one can observe that they are much lower. On the other hand, Deheyn and Latz using the 45% HNO_3 obtained the aluminium concentration at the level of 0.055 to 0.62 mg/g d.m. in the sediments of San Diego Bay, describing this form of aluminium as connected with organic matter [6].

The highest concentration of aluminium in the bottom sediments of the Mała Wełna River was determined in the lithogenic fraction (fraction V), in which aluminium is practically unavailable for living organisms. It results from the fact that aluminium is built in mineral structures, hence, in order to release it, strongly reductive conditions would be necessary. In the bottom sediments of the Mała Wełna River the content of aluminium in fraction V was in the range from 550 to 2330 mg/kg d.m., and the highest concentrations were observed for granulometric fraction < 0.063 mm (Fig. 6). These results are considerably lower than the ones obtained by Baborowska *et al.* where the total aluminium content in the bottom sediments was determined at the concentration level of 41–73 g/kg d.m. [1]. While analyzing the aluminium concentration in particular granulometric fractions of the investigated bottom sediments samples, the highest concentrations of aluminium were observed in fraction < 0.063 mm for chemical fractions II, IV and V, and for granulometric fraction > 2.0 mm in the case of chemical fraction III (Fig. 6). The similar trend of aluminium was observed in granulometric fraction of tsunami deposit samples determined by Zioła-Frankowska *et al.* [34].

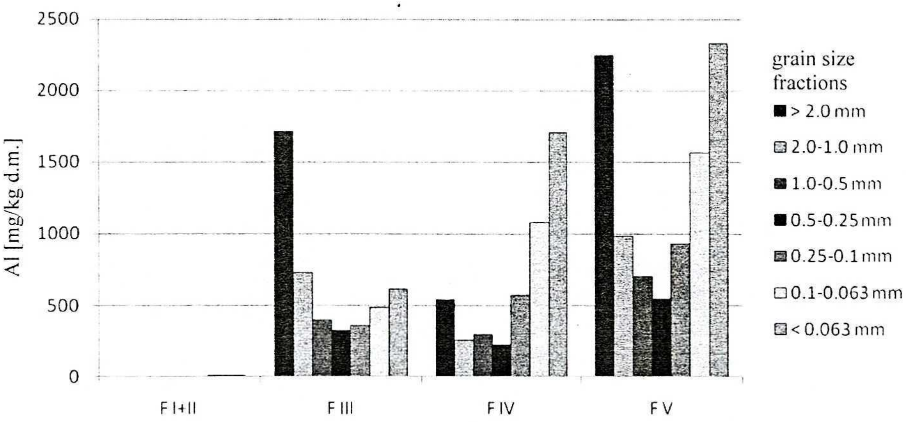

Fig. 6. Concentration of aluminium in bottom sediment of the Mała Wełna River, in particular chemical fraction and granulometric fractions (sampling point No. 5)

The results of the research by Sutherland *et al.* [28, 29] in granulometric fractions < 0.063, 0.063–0.125, 0.125–0.25, 0.25–0.5, 0.5–1.0, 1.0–2.0 mm indicate that author obtained a similar dependence of the tendency for one analyzed element (Pb) in comparison to the obtained results presented in this study. Sutherland determined the highest concentration of Pb in bottom sediments in the granulometric fraction 0.500–1.0 mm [28, 29]. Frankowski *et al.* presented the results of the research on bottom sediments of the Oder River, where the extraction with use of HNO_3 and H_2O_2 acids in twelve granulometric fractions of river sediments was applied [12]. The results of determination of metals for particular granulometric fractions presented in the study look similar to the results obtained in this study and in the study by Frankowski *et al.* [11, 13].

Within the scope of the conducted research, the assessment of the influence of the method of bottom sediments sample preparation on the aluminium concentration, in par-

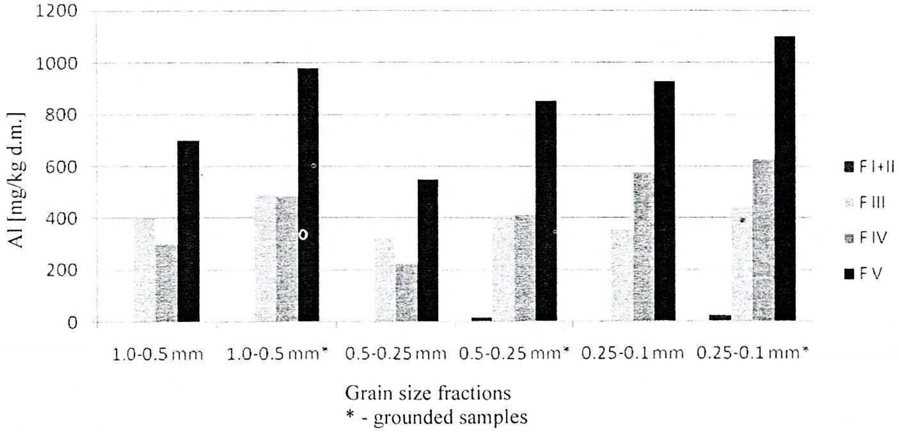

Fig. 7. Concentration of aluminium in particular chemical fractions for selected grain size fractions in bottom sediments of the Mała Wełna River (sampling point No. 5)

ticular chemical fractions subjected to the procedure of sequential extraction, was conducted. Sample No. 5 with 1.0–0.5 mm, 0.5–0.25 mm, 0.25–0.1 mm grain size fractions was subjected to the sequential extraction procedure for the samples grounded in the agate mortar, and for the samples which were not grounded (Fig. 7).

The obtained results indicate a considerably higher concentration of aluminium in chemical fractions III–V for the grounded samples, in comparison with the ones which were not grounded.

CONCLUSIONS

Based on the obtained results of the aluminium research in the samples of surface waters and bottom sediments of the Mała Wełna River in the period from May to August 2006, the following conclusions may be formulated:

1. Low concentrations of total aluminium (from 4.14 to 25.9 $\mu g/dm^3$) determined in the water of the Mała Wełna River indicate only a small burden of the investigated waters with this element. A slight increase of the aluminium concentration was only observed at the sites located below towns, which may indicate local contamination with this element.
2. It was also observed that, together with the increase of $[H^+]$ and sulphate ions concentration, the concentration of $AlSO_4^+$ and $Al(SO_4)_2^-$ complexes increases, with a simultaneous decrease of the total aluminium content. It was assumed that the dominating complex form in the all investigated water samples was $AlSO_4^+$.
3. For particular granulometric fractions of the all investigated samples of bottom sediments the highest concentration of aluminium was determined in fraction < 0.063 mm for chemical fractions II, IV, V and for granulometric fraction > 2.0 mm in the case of chemical fraction III.
4. In the case of bottom sediments, the lowest concentration of aluminium was determined in the exchangeable fraction and the fraction connected with carbonates (fraction I and II – the most mobile), while the highest concentrations were determined in the lithogenic fraction (fraction V), where aluminium is practically unavailable for living organisms.
5. The concentrations of aluminium speciation forms obtained in water ($AlSO_4^+$; $Al(SO_4)_2^-$) and in bottom sediments (especially for chemical fractions I and II) do not pose any danger for living organisms in the Mała Wełna River.
6. It was found that higher concentration of aluminium in chemical fractions III–V was observed for the grounded samples in comparison with the ones which were not grounded.

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REFERENCES

[1] Baborowski M., O. Buttner, P. Morgenstern, F. Kruger, I. Lobe, H. Rupp, W. Tumpling: *Spatial and temporal variability of sediment deposition on artificial-lawn traps in floodplain of the River Elbe*, Environmental Pollution, **148**, 770–778 (2007).

[2] Berthon G.: *Aluminium speciation in relation to aluminium bioavailability, matabolism and toxicity*, Coordination Chemistry Reviews, **228**, 319–341, (2002).

[3] Bi S.P., X.D. Yang, F.P. Zhang, X.L. Wang, G.W. Zou: *Analytical methodologies for aluminium speciation in environmental and biological review*, Journal Analytical Chemistry, **370**, 984–996 (2001).

[4] Boudot J.P., D. Merlet, J. Rouiller, O. Maitat: *Validation of an operational procedure for aluminium speciation in soil solutions and surface waters*, The Science of the Total Environment, **158**, 237–252 (1994).

[5] Christophersen N., C. Neal, R.D. Vogt, J. Esser, S. Andersen: *Aluminium mobilization in soil and streamwaters at three Norwegian catchments with differences in acid deposition and site characteristics*, Sci. Tot. Env., **96**, 175–188 (1990).

[6] Deheyn D.D., M. Latz: *Bioavailability of metals along a contamination gradient in San Diego Bay (California USA)*, Chemosphere, **63**, 818–834 (2006).

[7] Drabek O., L. Mladkowa, L. Boruvka, J. Szakowa, A. Nikodem: *Comparison of water – soluble and exchangeable forms of Al in acid forest soils*, Journal of Inorganic Biochemistry, **99**, 1788–1795 (2005).

[8] Driscoll C.T., K.M. Postek: *The chemistry of aluminum in surface waters. The environmental chemistry of aluminium*, 2nd edition, Garrison Sposito, 1996, 363–419.

[9] Driscoll C.T., W.D. Schecher: *The chemistry of aluminium in the environment*, Environ. Geochem. Health, **12**, 28–49 (1990).

[10] Frankowski M., Zioła-Frankowska A., Kowalski A., Siepak J.: *Fractionation of heavy metals in bottom seoliments Using Tessier procedure*, Euviron. Earth Scio, DOJ 10. 1007/s12665-009-0258-3 (2009).

[11] Frankowski M., M. Siepak, A. Zioła, K. Novotny, T. Vaculovič, J. Siepak: *Vertical distribution of heavy metals in grain size fractions in sedimentary rocks: Mosina-Krajkowo water well field, Poland*, Environmental Monitoring and Assesment, 155(1–4), 493–507 (2009).

[12] Frankowski M., T. Sobczyński, A. Zioła: The *Effect of Grain Size Structure on the Content of Heavy Metals in Alluvial Sediments of the Odra River*, Polish Journal of Environmental Studies, **14** (supl. 5), 81–86 (2005).

[13] Frankowski M., A. Zioła, M. Siepak: *Analysis of heavy metals in particular granulometric fractions of bottom sediments in the Mala Welna River (Poland)*, Polish Journal of Environmental Studies, **17**(3), 343–350 (2008).

[14] Guibaud G., C. Gauthier: *Aluminium speciation in the Vienne river on its upstream catchment (Limousin region, France)*, Journal of Inorganic Biochemistry, **99**, 1817–1821 (2005).

[15] Guibaud G., C. Gauthier: *Study of aluminium concentration and speciation of surface water in four catchments in the Limousin region (France)*, Journal of Inorganic Biochemistry, **97**, 16–25 (2003).

[16] Gworek B.: *Toxicity of aluminium in environment*, Ochrona Środowiska i Zasobów Naturalnych, **29**, 27–38 (2006).

[17] Kabata-Pendias A., H. Pendias: *Biogeochemistry of trace elements*, Polish Scientific Publishers PWN, Warsaw, 1999.

[18] Kondracki J.: *Regional geography of Poland*, Polish Scientific Publishers PWN, Warsaw, 2000.

[19] Kroglund F., B. Finstad: *Low concentration of inorganic monomeric aluminium impair physiological status and marine survival of Atlantic salmon*, Aquaculture, **222**, 119–133 (2003).

[20] Lawlor A.J., E. Tipping: *Metal in bulk deposition and surface waters at two unpland nlocations in northern England*, Environmental Pollution, **121**, 153–167 (2003).

[21] Matus P., J. Kubova: *Complexation efficiency fixed 8-HQS and salicylic acid ligands groups for labile aluminium species determination in soils – comparison of two methods*, Analytica Chimica Acta, **573-574**, 474–481 (2006).

[22] Matus P., J. Kubova: *Complexation of labile aluminium species by chelating resins Iontosorb – a new method for Al environmental risk assessment*, Journal of Inorganic Biochemistry, **99**, 1769–1778 (2005).

[23] Ruszczyńska A., K. Pyrzyńska, E. Bulska: *On the use of solid-phase extraction for the fractionation of aluminium species*, Chem. Anal. (Warsaw), **49**, 19–28 (2004).

[24] Sin S.N., H. Chau, W. Lo, L.M. Ng: *Assesment of heavy metal cations in sediments of Shing Mun River, Hong Kong*, Environment International, **26**, 297–301 (2001).

[25] Sobczynski T., M. Szwak, A. Ziola, J. Siepak: *Fractionation of aluminium from alluvial sediments*, Environment Protection Engineering, **30**(4), 177–182 (2004).

[26] Sobczynski T., A. Pelechata, A. Ziola, M. Pelechaty, L. Burchardt, J. Siepak: *Accumulation of aluminium in the freshwater ecosystem of Jaroslawieckie Lake*, Polish Journal of Environmental Studies, **11**, 172–182 (2002).

[27] Stutter M., R. Smart, M. Cresser, S. Langan: *Catchment characteristics controlling the mobilization and potential toxicity of aluminum fraction in the catchment of the River Dee, northeast Scotland*, The Science of Total Environment, **281**, 121–139 (2001).

[28] Sutherland R.A., F.M.G. Tack: *Sequential Extraction of Lead from Grain Size Fractionated River Sediments Using the Optimized BCR Procedure*, Water, Air, and Soil Pollution, **184**(1-4), 269–284 (2007).

[29] Sutherland R.A.: *Lead in grain size fractions of road-deposited sediment*, Environmental Pollution, **121(2)**, 229–237 (2003).

[30] Tessier A., P.G. Campbell, M. Bisson: *Sequential extraction procedure for the speciation of particulate trace metals*, Analitycal Chemistry, **51**(7), 844–851 (1979).

[31] Wauer G., H.J. Heckemann, R. Koschel: *Analysis of toxic aluminium species in natural waters*, Microchimica Acta, **146**, 149–154 (2004).

[32] Zioła A., T. Sobczyński: *The Effect of Water Ionic Composition on Liberation of Aluminium from Bottom Sediment*, Polish Journal of Environmental Studies, **14** (supl. V), 101–104 (2005).

[33] Zioła-Frankowska A., Frankowski M., J. Siepak: *Development of a new analytical method for online simultaneous qualitative determination of aluminium (free aluminium ion, aluminium-fluoride complexes) by HPLC-FAAS*, Talanta, **78**, 623–630 (2009).

[34] Zioła-Frankowska A., M. Frankowski, W. Szczuciński, J. Siepak: *Analysis of labile aluminium form in grain size fractions of tsunami deposits in Thailand*, Polish Journal of Environmental Studies, **18**, 77–85 (2009).

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OZNACZANIE I MODELOWANIE GLINU W POŁĄCZENIACH Z SIARCZANAMI W WODACH POWIERZCHNIOWYCH I FRAKCJONOWANIE GLINU W OSADACH DENNYCH

W pracy przedstawiono wyniki oznaczeń glinu w próbach wód powierzchniowych i osadach dennych rzeki Mała Wełna. W wodach powierzchniowych stwierdzono stężenie glinu w przedziale 4,14–25,9 $\mu g/dm^3$. Przy wykorzystaniu programu do modelowania Mineql+ wyliczono stężenie form kompleksów glinowo-siarczanowych w badanych próbkach wody. Frakcjonowanie glinu w osadach dennych przeprowadzono we frakcjach granulometrycznych o uziarnieniu: > 2,0; 2,0–1,0; 1,0–0,5; 0,5–0,25; 0,25–0,1; 0,1–0,063; < 0,063 mm, z wykorzystaniem zmodyfikowanego schematu ekstrakcji sekwencyjnej zaproponowanego przez Tessiera i współpracowników. Najniższe stężenia glinu występowały we frakcji granulometrycznej od 0,25–0,5 mm, natomiast najwyższe stężenia we frakcji 0,1–0,063 mm i < 0,063 mm. Zaobserwowano również wzrost stężenia glinu we frakcji granulometrycznej > 2,0 mm. W przypadku frakcji chemicznych najniższe stężenia glinu oznaczono we frakcji wymienialnej i związanej z węglanami (frakcja I i II), natomiast najwyższe stężenia glinu oznaczono we frakcji litogennej (frakcja V). Porównano metody przygotowania próbki do analizy glinu w osadach dennych. Stwierdzono wyższe stężenia glinu w próbkach poddanych rozcieraniu bez względu na wielkość frakcji granulometrycznej. Glin w wodach powierzchniowych oznaczono techniką absorpcyjnej spektrometrii atomowej z atomizacją w kuwecie grafitowej (GF-AAS), a w osadach dennych techniką absorpcyjnej spektrometrii atomowej z atomizacją w płomieniu (F-AAS).