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SPECIATION OF ALUMINIUM IN THE WATER AND BOTTOM
SEDIMENT OF FISH-BREEDING PONDS

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Abstract: Water and bottom sediment samples collected from a few fish-breeding ponds/reservoirs were subjected to tests. The aim of this paper was to determine the total content of aluminium and its fractions in the samples tested to estimate the potential risk to fish caused by the toxic forms of aluminium. The monomeric inorganic aluminium in waters was determined using the ion exchange and extraction-colorimetric method with oxyquinoline according to Barnes's-Driscoll's procedure. The bottoms were fractionated using a three-step sequential extraction procedure and the microwave mineralisation. The total content of aluminium in waters and extracts was determined using the spectrophotometric method with eriochromocyanine R, and comparatively using the ICP OES technique. The results were subjected to statistical analysis. The level of concentration of labile Al in the waters about 26–34 $\mu\text{g}/\text{dm}^3$ and content of exchangeable Al 5–34 mg/g range in bottom sediments are possibly hazardous to aquatic organisms.

INTRODUCTION

Aluminium is one of the main components that constitute the Earth's crust and takes the third place following oxygen and silicon. It occurs mainly in the form of aluminium silicates and in the case of erosion, aluminium becomes a soil component. The acidity of soils caused by nitric oxides found in the atmosphere and industrial sulphur, as well as their emission to the Earth's surface facilitates the release of aluminium ions from soil and their migration to surface and underground waters [1, 2].

In the past aluminium was considered completely harmless to water organisms. After revealing some cases of rapid decrease in fish population and even a complete extinction of some species in lakes of the United States and Europe, mainly southern Scandinavia, the toxicity of Al towards fish has been recognized [3]. The impact of aluminium released from acidified soils on the life of fish and other water organisms has been the subject of intense study for the last three decades because of evidence linking atmospheric deposition of acidic rain with declines in freshwater fish population [4]. The investigations proved that aluminium in acidified soil solutions is subject to chemical reactions with other ions, thus creating inorganic and organic monomeric complexes, then as a result of polymerisation, it creates high-molecular compounds that migrate to natural waters.

In water environment one can find the fractions of dissolved aluminium, colloidal aluminium and sediments. Dissolved aluminium occurs in acidic surface waters primarily as the free Al ion and complexed with hydroxide, fluoride, and organic ligands. Driscoll [5] concluded that only inorganic forms of Al were toxic to postlarvae of brook trout and white sucker. The presence of toxic forms of aluminium depends primarily on the pH and the Al total concentration of the surface water, but is also affected by other ion concentrations (e.g. calcium, phosphorous) and organic matter as well as temperature and exposure period [6, 7].

The most reactive and toxic forms of aluminium found in water environment are: Al^{3+} , $\text{Al}(\text{OH})_2^+$, $\text{Al}(\text{OH})_3^0$ and very unstable complexes of aluminium, mainly inorganic ligands. All the forms of aluminium belong to the category of the so-called monomeric inorganic aluminium. In natural water reservoirs aluminium occurs at concentrations below 1 mg/dm^3 , however the presence of the above-mentioned toxic form of aluminium even at trace quantities can be risky to some fish species. Literature reports suggest that pH values in the range of 4.2 to 5.6 and Al concentration higher than $0.1\text{--}0.2 \text{ mg/dm}^3$ may lead to the death of trout [8]. In Poland, it was revealed that the critical limit amounts to 0.070 mg Al/m^3 [9]. Two major mechanisms of the Al toxicity are suggested: (1) an electrolyte loss possibly induced by an interaction of inorganic monomeric Al with enzymes, and (2) the cytotoxicity of labile-Al to the gill epithelia resulting in the impairment of gas exchange. At higher pH levels these effects decrease in intensity whereas mucification increases, an effect which seems to be induced mainly by accumulating polymeric Al [8]. Gardner and Comber's study [10] showed a minimum concentration of reactive aluminium at pH value of approximately 6.8, coinciding with the prevalence of non-reactive, insoluble $\text{Al}(\text{OH})_3$ species. Below this pH value, the more soluble reactive $\text{Al}(\text{OH})_2^+$ and Al^{3+} species are more important. Above pH 6.8, the importance of $\text{Al}(\text{OH})_4^-$ increases (also reactive species). At pH values of 8 and higher $\text{Al}(\text{OH})_4^-$ constitutes more or less 100% of dissolved aluminium species.

Aluminium is mobile and migrates easily from water to sediments and back, especially while pH values change. Therefore, the assessment of potential risk to water organisms by toxic aluminium requires speciation analysis both in water and in bottom sediments [11].

Over the recent twenty years there have been published many papers on the investigations of aluminium speciation. To determine aluminium hydroxycomplexes $\text{Al}(\text{OH})_2^+$, $\text{Al}(\text{OH})_3^0$, $\text{Al}(\text{OH})_4^-$, complexes of aluminium with amines, aluminium phosphate complexes in soil solutions as well as in surface waters, scientists use the NMR spectroscopy (^{27}Al NMR, ^1H NMR, ^{13}C NMR, ^{31}P NMR), Fluorescent Spectroscopy and IR, which allow them to determine a content of aluminium complex with fulvic and huminic acid in aqueous solutions. In addition to the above-mentioned spectroscopic methods there are also other methods that make it possible to determine various forms of aluminium, which include chromatography used in combination with mass or optical spectroscopy methods [12] and UV photometry [13, 14], cation exchange fast protein liquid chromatography with electrothermal atomic absorption spectrometry [14] and Flame Atomic Absorption Spectrometry e.g. HPIC-FAAS [15–17]. However, the determination of individual Al species is very difficult owing to their low concentration level, the presence of a complex matrix, mostly of organic origin, and the dynamic equilibrium among different Al species in natural samples.

The complexity of the Al speciation analysis has forced researchers to develop the operational speciation to distinguish between broad groups of Al species. Speciation of Al is achieved by kinetic or thermodynamic based measurements. The species determined are referred to as 'labile', 'total monomeric', 'inorganic monomeric', 'fast reaction' Al, etc. [18–20]. The Barnes's and Driscoll's procedure is one of the most popular methods of aluminium operational speciation in water [21, 22]. It consists in separating three groups of aluminium compounds reacting directly with a specified dye, this is the so-called reactive aluminium, compounds reacting at pH = 1 within several minutes – reactive aluminium in acids and non-reacting compounds – non-reactive aluminium, which is not subject to ion exchange in a cation exchanger. Each of the three groups has a number of individual components, whose differentiation is not important from the point of the toxicology of natural water reservoirs, however, it is important to determine the so-called monomeric inorganic aluminium, whose presence results in toxic impact on water organisms. In each fraction the aluminium content is determined using spectrophotometry with pyrocatechol violet or 8-hydroxyquinolsulphonic acid. The Driscoll's method has a lot of modifications and improvements, nonetheless, the very principle of aluminium fractionation remains unchanged, which presents the Table 1 [23].

Table 1. Fractionation of aqueous aluminium [23]

Sample treatment	Aluminium fraction	Fraction composition
Acid digestion	Total reactive (Al_t)	Acid soluble forms
Without digestion	Total monomeric (Al_m)	Inorganic and organic, monomeric complexes
	Acid soluble ($Al_t - Al_m$)	Colloidal, polymeric and strong organic complexes
Cation-exchange treatment	Non - labile monomeric (Al_o)	Monomeric organic complexes
	Labile monomeric ($Al_m - Al_o$)	Al^{3+} , hydroxide, sulphate, fluoride complexes

Liu [24] studied the voltammetric fractionation of Al using Pyrocatechol Violet (PCV). The labile monomeric Al fraction, which is thought to be the toxic fraction, is directly measured at pH = 4.8 (0.20 mol/dm³ NaOAc–HOAc). The total monomeric Al fraction is measured at pH = 8.5 (0.20 mol/dm³ NH₃·H₂O–NH₄Cl). The concentrations of the other fractions, total acid reactive Al, total monomeric Al, organic monomeric Al and acid soluble Al are also measured directly or indirectly. The method compared well with Driscoll's 8-hydroquinoline extraction/ion exchange method.

The operationally defined procedures for the aluminium fractionation in the bottom sediments are single-step extraction or sequential extraction using solutions with gradually growing aggressiveness. In the single-step extraction KCl solution 1 M is often used, and the fraction obtained Al_{KCl} reflexes the presence of potentially toxic aluminium forms [25]. Other extracting solutions are applied to sediment samples one-step extraction: H₂O, CaCl₂, Na₂S₂O₄, NH₄F, (NH₄)₂C₂O₄, HCl, NTA, EDTA, DTPA [26]. In the sequential extraction each stage provides a fraction related to specified

aluminium connections with known properties. The first methodology of sequential extraction was developed by Tessier, Campbell and Bisson [27] in 1979. This methodology was subject to many modifications [28, 29] and currently an operational five-step or three-step SEP proposed by the European Community Bureau of Reference (BCR) was used. In the BCR-endorsed procedure, the following fractions are taken into account: exchangeable, bound to carbonates, bound to iron and manganese oxides, bound to organic matter, and residual. In the three-stage procedure, the first two are termed an acid-soluble phase [30]:

Fraction 1. Acid-extractable (Exchangeable and weak acid soluble)

Aluminium adsorbed on the surface of solids. As a result of changes in ionic water composition, the shift in balance in the system sorption-desorption can reach water resources.

Fraction 2. Reducible

Aluminium adsorbed on the surface of precipitating hydrated iron and manganese oxides. As a result of iron and manganese reduction, the sediment can be dissolved and aluminium can return to the solution.

Fraction 3. Oxidizable

Aluminium adsorbed on the surface of organic matter or built-in the matter.

Standardised three steps sequential extraction was tested several times using reference materials [31] and compared with other fractionating procedures with success [32].

Another proposal is the use of sequential microwave extraction that considerably reduces the time of analyses, reduces the consumption of reagents and electric power. The microwave method according to the scheme proposed by Pérez-Cid [33] also distinguishes three aluminium fractions, however here we use different extraction solvents than in the case of Tessier's procedure. The comparison of traditional Tessier's method with microwave methods according to the Pérez-Cid scheme and using reagents used in the Tessier's procedure have been included in the paper [34].

The paper presents the investigations on aluminium fractionation in waters and sediments of selected fish-breeding reservoirs. The aim of the paper was to determine the concentration of toxic to fish aluminium forms to estimate the potential risk to fish breeding and aquatic life which has not been determined so far.

METHODOLOGY

Water and bottom sediments from four fish-breeding reservoirs were subject to testing.

Using the spectrophotometric method with eriochromocyanine R performed in accordance to PN-92/C-04605/02 standard, the following values were determined:

Al_t – total Al - the total content of aluminium including colloids and suspended matters in non-filtered samples fixed with nitric acid to $pH = 2.0$;

Al_{mc} – acid soluble Al (monomeric and colloidal Al) – aluminium determined in a filtered sample fixed with nitric acid to $pH = 2.0$.

Using the extraction-colorimetric Barnes's-Driscoll's method with 8-oxychinoline the following values were determined:

Al_m – monomeric Al – the sum of non-labile and labile forms of aluminium (organic and inorganic).

Separating the inorganic forms using the ion exchange Barnes's-Driscoll's method with oxychinoline allowed us to determine:

Al_o – non-labile Al – monomeric organic aluminium.

Then the following values were calculated:

Al_i – labile Al – monomeric inorganic aluminium.

$$Al_i = Al_m - Al_o$$

Al_c – colloidal Al

$$Al_c = Al_{mc} - Al_m$$

Al_s – suspended Al

$$Al_s = Al_t - Al_{mc}$$

The bottom sediments were subject to sequential extraction according to the standardised three-step SEP by traditional methods and using microwaves. Both methods differed in the conditions of process course but shared the same extraction solvents. The fractions obtained from the both methods mentioned above were subject to analysis using the spectrophotometric method UV-VIS and comparatively ICP-OES. The results obtained were checked using a statistical analysis.

The last stage covered the determination of the forms of aluminium in water acidified to pH = 4.3. Such a procedure was supposed to check how the concentration of particular forms of aluminium changes, especially the changes of toxic aluminium contained in water as a result of acidification of the environment.

Collection and initial preparation of samples

The samples were taken from 4 different fish-breeding reservoirs:

Reservoir 1 – the so-called commercial pond, located in the centre of PAN (Polish Academy of Science) in the Institute of Ichthyobiology and Aquaculture in Gołysz;

Reservoir 2 and 3 – natural fish ponds in the Municipality of Koszęcin, restocked;

Reservoir 4 – artificial fish-breeding pond under operation in Woźniki Śląskie.

Water samples collection was performed in July according to PN-ISO 5667-4 standard. Samples (2 dm³) were taken in five places from the depth of about 10–40 cm and 100–200 cm away from shore and averaged. The temperature and pH of the averaged samples were measured using a pH-meter manufactured by Elmetron with electrode EPP-2, and then the samples were fixed by acidification to pH = 2 (durable for 1 month) or freezing to -20°C.

The collection of bottom sediments was performed in accordance with PN-ISO 5667-15 standard. The commercial pond samples c.a. 2 kg were taken from six places in October after emptying the pond and blended. The natural ponds samples were collected in July from the five water bottom points (the same as water samples) and carefully mixed. The samples were placed in proper plastic containers to save their natural properties. Air-dry sediment was mixed and passed through a sieve with a mesh of 100 μm. From the above-described sediments samples for the analysis were collected.

Analytical methods

The content of aluminium was determined using spectrophotometric method with R eriochromocyanine in accordance with the PN-92/C-04605/02 standard within the concentrations range of 0.04–1.0 mg/dm³ at a wavelength of λ = 535 nm, using a cuvette with an absorptive layer thickness of 5 cm. Concentrations of other elements,

including aluminium in water under examination, were determined with the ICP OES method.

Reagents applied: ascorbic acid, solutions 0.2% (m/m); nitric acid (V) with $d = 1.48 \text{ g/cm}^3$, sulphuric acid (VI) with $d = 1.84 \text{ g/cm}^3$, 0.05 mol/dm^3 , (1+1); ammonia water (1+6); acetate buffer with $\text{pH} = 6.0$, R eriochromocyanine R, basic solution with $\text{pH} = 2.9$, working solution (1+4); potassium-aluminium sulphate, basic standard solution, 0.5 mg Al/dm^3 , working standard solution 0.02 mg Al/dm^3 ; methyl orange – indicator, solution 0.1%.

Equipment used:

Spectrophotometer UV–VIS manufactured by Varian Cary 50 Scan;
Spectrometer ICP-OES manufactured by Varian 710.

Determining the total Al and acid soluble Al in water samples

Total aluminium content – Al_t – was determined using the spectrophotometric method with R eriochromocyanine R after mineralising the samples with concentrated acids: sulphuric(VI) and nitric(V) according to the description presented in the Polish Standard (PN-92/C-04605/02). The total content of aluminium, both monomeric and colloidal – Al_{mc} – was determined in water samples passed through a $0.45 \mu\text{m}$ filter, and mineralised in the way described above. A part of the samples was mineralised with concentrated nitric acid using microwave US EPA 3015 Method, and in some mineralised samples other chemical elements were determined using either the ICP-OES.

Determining the monomeric Al in water samples using the Barnes's – Driscoll's extraction-colorimetric method with oxochinoline

Reagents used: hydroxylamine hydrochloride solution 20%; phenantroline-1,10, solution 1%; 8-hydroxyquinoline, solutions 5%; phenol red, ammonia, solution 25 mol/dm^3 ; buffer solution with $\text{pH} = 8.3$; methyl-2-pentanone (MIK), standard solution of aluminium obtained from metallic aluminium, 1 g/dm^3 .

Performing the determination

500 cm^3 of sample was taken to a separator, 10–15 drops of phenol red was added, plus 2 cm^3 5% of 8-hydroxyquinoline and the mixture was stirred vigorously. Drops of 10 mol/dm^3 NH_4OH were added until the solution changed its colour into red ($\text{pH} = 8$), then 5 cm^3 of buffer and 15 cm^3 of MIK were added, the mixture was stirred for 10 seconds. The water layer was removed, whereas the organic layer was subject to mineralisation: the sample was evaporated and then 10 cm^3 of concentrated sulphuric acid was added and the mixture was heated until carbonisation. After cooling down the solution 20 cm^3 of concentrated nitric acid was added and the solution was heated until discolouration. The entire mixture was evaporated almost dry, and after adding 10 cm^3 of concentrated nitric acid, heated until boiling, cooled down, and then filtered into a 25 cm^3 flask and filled with demineralised water up to the mark. The experiment was repeated 3 times. The samples prepared were subject to spectrophotometric analysis.

Determining the non-labile Al in water samples with ion exchange method

Reagents used: hydrochloric acid 1 mol/dm^3 ; sodium chloride 1 mol/dm^3 ; Amberlite IR 120 (strong acid cation exchange resin type polystyrene sulphonate).

Performing the determination

The separation was performed in an ion exchange column with an inner diameter of 10 mm. Volume of the ion exchange bed (Amberlite IRA 120) equalled to $BV = 10 \text{ cm}^3$. The resin was conditioned: $50 \text{ cm}^3 1 \text{ mol/dm}^3 \text{ HCl}$ and $50 \text{ cm}^3 1 \text{ mol/dm}^3 \text{ NaCl}$ at a flow rate of $V = 4 \text{ cm}^3/\text{min}$., and then with water. The sample was separated in the column at a maximum flow rate of $4\text{--}5 \text{ cm}^3/\text{min}$. In the output the content of aluminium A₀ (monomeric organic) was determined using the extraction-colorimetric Barnes's-Driscoll's method with oxychinoline in the way described above. Three trials were performed for each water under investigation.

Sequential analysis of Al in bottom sediment samples

Reagents used: acetic acid, solution 1 mol/dm^3 ; hydroxylamine hydrochloride, solution 0.1 mol/dm^3 ; hydrogen peroxide, 30% (m/m); ammonium acetate, solution 1 mol/dm^3 .

Equipment

Wavershaker MLL 547 manufactured by AJL Electronic (Poland)

Microwave mineraliser MARS 5 manufactured by CEM Co. (Matthews).

The samples were subject to three-step sequential extraction using both traditional and the microwave method.

The three-step sequential extraction procedure

Samples weighing 5 grams were taken for extraction and as a result three fractions were obtained:

Fraction 1 – shaking the bottom sediment for 4 hours in $50 \text{ cm}^3 0.1 \text{ M}$ of acetate acid and separation by centrifuging and passing through a filter.

Fraction 2 – shaking the sediment from fraction 1 for 4 hours in 0.1 M of hydroxylamine hydrochloride and separation by centrifuging and filtering.

Fraction 3 – covering the sediment from 2 fractions with $50 \text{ cm}^3 30\%$ hydrogen peroxide, and leaving it for 1 hour, then heating for 1 hour at a boiling point and cooling down for another hour. Adding $50 \text{ cm}^3 1.0 \text{ M}$ of ammonium acetate and leaving the solution for 4 hours.

The three fractions obtained were subject to spectrophotometric analysis with R eriochromocyanine. For reference (comparison) the ICP OES method was used. Three parallel series were performed.

Microwave three-step sequential extraction procedure

Samples of bottom sediments weighing 0.5 g each were taken to teflon microwave dishes placed in the carousel of Mars mineraliser, then the same reagents were added as for the traditional method. The samples after putting into the microwave furnace were subject to microwave power of 1280 W and held there for 10 minutes at 170°C . As a result the same three fractions as above were obtained.

Determining the forms of Aluminium in acidified water samples

The pond water with bottom sediments from fish pond 2 was acidified to $\text{pH} = 4.3$ and left for the period of three weeks to determine a new balance water/sediment in the environment more acidic than in real amounting to $\text{pH} = 7.13$. After three weeks a speciation analysis of aluminium in water was performed using the above-described methods.

Statistical analysis

The results obtained for the concentration of aluminium in water and bottom sediments were subjected to statistical analysis. We used Dixon's test that allowed us to detect a result burdened with a gross error, then the results were analysed using t-Student distribution.

RESULTS

The samples were taken from 4 different fish-breeding reservoirs located in unpolluted areas. After measuring pH, the water samples were subjected to speciation analysis to determine the total aluminium content (including the sediment), monomeric and colloidal (from the filtered sample), monomeric aluminium (organic and inorganic) and monomeric organic aluminium. The remaining concentrations of aluminium forms (monomeric inorganic, colloidal and suspended forms) were calculated based on correlations presented above. The results are shown in Table 2.

Table 2. Fractions of aluminium in the water of fish-breeding pond determined with the use of spectrophotometric and the ICP-OES method

Fractions of aluminium	Concentration of aluminium $C \pm t s / \sqrt{n}$ [$\mu\text{g}/\text{dm}^3$]					
	Water 1 Gołysz	Water 2 Koszęcin		Water 3 Koszęcin	Water 4 Woźniki Śl.	
	pH=7.3	pH=7.13	Water acidified to pH=4.3		pH=8.12	pH=8.22
	Spectrophotometric method		ICP-OES method		Spectrophotometric method	
Al_t – total Al	115 ± 1	105 ± 1	3400 ± 190	3110 ± 410	89 ± 2	134 ± 3
Al_{mc} – acid soluble Al	88 ± 5	84 ± 8	2600 ± 310	1400 ± 110	62 ± 7	102 ± 3
Al_m – monomeric Al	60 ± 4	64 ± 5	310 ± 40	240 ± 40	23 ± 4	60 ± 4
Al_o – non-labile Al	26 ± 7	36 ± 5	50 ± 10	80 ± 10	20 ± 3	34 ± 3
Al_s – suspended Al	27 ± 3	25 ± 1	800 ± 110	1710 ± 40	26 ± 4	32 ± 3
Al_l – labile Al	34 ± 2	28 ± 2	260 ± 20	160 ± 30	3 ± 4	26 ± 2
Al_c – colloidal Al	28 ± 3	16 ± 1	2290 ± 240	1200 ± 10	39 ± 2	41 ± 3

t – coefficient taken from t-Student distribution tables for $\alpha=0.05$, $n=3$, $t=4.303$

s – average standard deviation

n – number of trials

C – concentration of aluminium (arithmetic average from n trials)

Table 3 contains a list of elemental analysis of water with the use of ICP-OES method.

The three-step SEP was performed at room temperature and at 80°C in the shaker, whereas the microwave method for bottom sediment samples was performed using a high-pressure and high-temperature (175°C) MARS microwave mineraliser at a microwave power of 1400 W. The results of aluminium levels in particular fractions are presented in Table 4.

DISCUSSION OF RESULTS

The analysis of water with the ICP-OES method shows that waters under investigation contain very high and high concentrations of the following elements: Ca, S, Mn, Si, Mg, Na, K, respectively: 37.2, 14.1, 8.2, 6.2, 4.0, 2.8 and 2.5 mg/dm³, within a range of 0.1–1.0 mg/dm³: P, Fe, Pb, Sr and Zn, whereas the other elements occur at concentrations below 0.1 mg/dm³ – see Table 3. The results presented above confirm the presence of high concentrations of silicates, sulphates and compounds of calcium, iron and magnesium in water taken from the ponds under investigation, which is confirmed by data found in the literature, according to which, the average concentration of sulphates amounts to 0.1 mol/dm³, whereas silicates reach the value of 0.3 mol/dm³ [35, 36].

The waters tested contain from 0.088 to 0.134 mg/dm³ total aluminium, which also corresponds to the data obtained from the literature on average concentrations of aluminium compounds in natural water reservoirs [7, 10, 24, 37]. The concentrations determined for the form of aluminium showing the highest toxicity to fish, the so-called

Table 3. Concentration of elements in pond water determined with the ICP-OES method

Pond no. 1 – commercial pond in Golysz, water pH = 7.3

Pond no. 2 – fish-breeding pond in Koszęcin, water pH = 7.13

Pond no. 3 – fish-breeding pond in Koszęcin, water pH = 8.12

Pond no. 4 – fish-breeding pond in Woźniki Śląskie, water pH = 8.22

Element/ wavelength [nm]	Concentration of element in water [mg/dm ³]			Element/ wavelength [nm]	Concentration of element in water [mg/dm ³]		
	Pond 2	Pond 3	Pond 4		Pond 2	Pond 3	Pond 4
Sb 206.834	0.0031	0.0018	0.0014	Ce 418.659	0.0002	0.0001	0.0031
B 249.772	0.0258	0.0237	0.0193	Gd 342.246	0.0011	0.0011	0.0014
Ge 209.426	0.0052	0.0011	0.0045	La 333.749	0.0044	0.0041	0.0034
P 213.618	0.5922	0.5294	0.5394	Pr 417.939	0.0077	0.0082	0.0064
Si 251.611	6.178	5.891	4.315	Th 283.730	0.0098	0.0104	0.0078
S 181.972	14.115	14.711	14.980	Rh 343.488	0.0002	0.0020	0.0016
Ti 336.122	0.0055	0.0043	0.0001	Au 242.794	0.0202	0.0183	0.0140
Sn 189.925	0.0006	0.0015	0.0025	Te 214.282	0.0030	0.0040	0.0010
Cd 214.439	0.0020	0.0013	0.0002	Al. 396.152	0.4233	0.4085	0.1721
Cr 267.716	0.0013	0.0013	0.0007	As 188.980	0.0069	0.0037	0.0021
Fe 238.204	0.1155	0.10885	0.0867	Ba 455.403	0.0206	0.0154	0.0141
Pb 220.353	0.1220	0.0940	0.0010	Bi 223.061	<0.0010	<0.0010	0.0191
Mn 257.610	8.247	7.652	5.624	Li 670.783	0.0041	0.0033	0.0015
Ni 231.604	0.0022	0.0023	0.0010	K 766.491	2.518	1.608	1.101
Tl 190.794	0.0017	0.0028	0.0040	Mg 279.553	4.034	3.718	2.813
Zn 213.857	0.1539	0.1425	0.0145	Na 589.592	2.801	2.590	2.034
Ca 422.673	37.173	38.203	33.758	Sr 407.771	0.1358	0.1236	0.0900

Table 4. Concentrations of aluminium in particular bottom sediment fractions determined with the use of spectrophotometric method

Bottom sediment fractions	Concentration of aluminium $C \pm t \cdot s / \sqrt{n}$ [mg/g]	
	Traditional method	Microwave method
Fish pond 1 Golysz		
Fraction 1 Acid-extractable	4.8 ± 0.9	12 ± 1
Fraction 2 Reducible	3.7 ± 0.5	42 ± 9
Fraction 3 Oxidizable	0.70 ± 0.03	39 ± 5
Fish pond 2 Koszęcin		
Fraction 1 Acid-extractable	34 ± 9.5	34 ± 4
Fraction 2 Reducible	2.8 ± 0.2	42 ± 4
Fraction 3 Oxidizable	0.46 ± 0.03	30 ± 7
Fish pond 3 Koszęcin		
Fraction 1 Acid-extractable	5.4 ± 0.6	9.3 ± 0.7
Fraction 2 Reducible	2.6 ± 0.6	8.4 ± 1.5
Fraction 3 Oxidizable	1.0 ± 0.1	12.9 ± 0.2
Fish pond 4 Woźniki Śl.		
Fraction 1 Acid-extractable	8.6 ± 0.7	24 ± 2
Fraction 2 Reducible	14 ± 1	46 ± 3
Fraction 3 Oxidizable	0.95 ± 0.03	30 ± 2

t – coefficient taken from t-Student distribution tables for $\alpha=0.05$, $n=3$, $t=4.303$

s – average standard deviation

n – number of trials

C – concentration of aluminium (arithmetic average from n trials)

monomeric inorganic aluminium, for particular ponds 1–4 equals to, respectively: 0.034, 0.028, 0.003 and 0.026 mg/dm³. The above-listed results are for water with actual pH value ranging from 7.13 to 8.22, so showing a slight alkaline reaction. The literature shows [7, 10] that in waters with pH = 6.2–8.0 the predominant form of aluminium is Al(OH)₃, whereas at pH > 8 it is mainly Al(OH)₄⁻, which may be also toxic to fish. However, acidification of water can be more dangerous. The tests performed at reduced water pH in pond 2 (The water was artificially acidified with acetate acid to pH = 4.3 and left for a period of 3 weeks in contact with bottom sediments) show a considerable increase in the concentration of all aluminium forms determined, including the most toxic to fish – inorganic monomeric aluminium, whose concentration grows by over 10 – times (Table 2). Such high concentrations of aluminium and low pH values can result in osmotic disturbances and reduced activity of some enzymes in fish and may become the main reason for their extinction [38]. At pH values below 5 water contains mainly Al³⁺, i.e. actually an octaedral hydride complex [(Al(H₂O)₆] [39] and the complexes of Al(OH)₂²⁺ and Al(OH)₂⁺, which can penetrate the organisms of fish through gills, where they accumulate in very large quantities and block the processes of ionic exchange and

respiration [40]. In addition to this, in acidic waters aluminium hydroxide is subject to polymerisation creating Al_{13} compound, which is also considered toxic to fish [38].

The results of aluminium concentrations subject to statistical analysis using the t-Student test are not exposed to gross errors as for an analysis of environmental samples. ICP-OES is a very universal and quick method, the results obtained are comparable to the spectrophotometric method. The difference between the results of aluminium levels obtained by the ICP-OES and spectrophotometric method amounts to a few percent (Table 2).

The sediments accumulating on the bottom of ponds gather various contaminations, including various forms of aluminium. Because of their physical and chemical properties, it is very easy for aluminium to pass to solids, and its numerous forms, especially hydroxycomplexes along with changes in pH modify their solubility and are subject to precipitation or co-precipitation in bottom sediments [41, 42].

The samples of bottom sediments taken from four different fish-breeding ponds differ considerably in aluminium content found in particular fractions (Table 4). It means that the sites feature different geological structures and differ in a variety of aluminium forms related to the bottom sediments. Comparing the results of aluminium levels determined in particular fractions of bottom sediments obtained using a traditional method, the highest concentration of aluminium was observed in fraction 1 – the so-called acid-extractable (exchangeable and weak acid soluble), which represents the most mobile aluminium form (free aluminium ion Al^{3+} , aluminium fluoride complexes $AlF_n^{(3-n)+}$ [16], aluminium hydroxy complexes $Al(OH)_n^{(3-n)+}$ and other inorganic forms), as being only adsorbed on the surface of solids. In fraction 2 – the so-called reducible one, we noted a lower content of aluminium than in fraction 1 except for bottom sediment 3, in which fraction 2 contained the highest share of aluminium (60.3%). Fraction 2 contains the forms of aluminium combined with iron and manganese oxides. The remaining fraction number three, the so-called oxidizable one, which represents aluminium built in organic matter, features the lowest mobility and has the lowest share ranging from 0.5 to 7.4%.

The results obtained in the microwave extraction method with the same reagents as used in the traditional procedure show a considerably higher concentration of aluminium in particular bottom sediment fractions. Considerably higher concentrations are obtained in fractions 2 and 3. The reason for this can be different extraction conditions, such as higher process temperature, pressure and the influence of microwaves. The microwave method allows for a more thorough extraction of aluminium as compared with the traditional method, predominantly in the case of more resistant aluminium compounds e.g. with silicates or organic matter, however, the statement that this procedure gives the correct information on the bioavailability of aluminum is controversial and requires further study.

CONCLUSION

- Analysis of water in fish breeding reservoir Gołysz showed low levels of labile forms of aluminum ($34 \mu\text{g}/\text{dm}^3$). Presumably this is due to the annual draining of the pond bottom and liming, which maintain the pH of water and bottom sediment at a satisfactory level of about 7.
- The acidity of water in the natural fish ponds, in which water is not treated, the bottom is not limed and also food is not supplied for the fish, was close to neutral or slightly

alkaline $7.1 < \text{pH} < 8.3$. The concentration of toxic forms of aluminum did not exceed the value toxic to fish and was $3\text{--}28 \mu\text{g}/\text{dm}^3$.

- The concentration of various elements in all investigated waters of commercial and natural ponds was similar to results found in other areas. The lowest concentration of accompanying elements was found in pond 4 (Woźniki Śląskie), which is a pond created by excavation of aggregates. Probably the pollutions present in water have been sorbed on aluminosilicates contained in the bottom sediment.
- Acidification of the portion of water and sediment from the natural pond to the pH of 4.3 in the laboratory and leaving it for 3 weeks resulted in a 10-fold increase in the concentration of labile aluminum in water, which is a dangerous condition for fish breeding.
- Bottom sediments differed in composition and appearance depending on the place of collection (breeding pond, natural and artificial). The content of mobile aluminum in the sediment was small and was within the range $5\text{--}34 \mu\text{g}/\text{g}$. Changing the acidity of the water caused a transition of alumina present in the sediment to the form of soluble Al and increase of toxic aluminium concentrations in the water.
- Annual liming of pond bottoms protects against a decrease of pH, while the natural ponds have no such safeguards and periodically occurring acidification can cause fish death. It is necessary to check water pH in fish-breeding ponds, whereas at reduced values, the pH should be properly adjusted.

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SPECJACJA GLINU W WODZIE I OSADZIE DENNYM STAWÓW RYBNO-HODOWLANYCH

Badaniom poddano próbki wody i osadu dennego pobrane z kilku stawów rybnych. Oznaczono całkowitą zawartość oraz frakcje glinu w badanych próbkach. Glin monomeryczny nieorganiczny wyznaczono metodą wymiany jonowej i ekstrakcyjno-kolorymetryczną z zastosowaniem oksychinoliny według procedury Barnes'a-Driscoll'a. Frakcjonowanie osadów dennych wykonano procedurą ekstrakcji sekwencyjnej Tessier'a w wersji ujednoliconej oraz z zastosowaniem mineralizacji mikrofalowej. Glin całkowity w wodzie oraz w ekstraktach oznaczono metodą spektrofotometryczną z eriochromocyjaniną R, porównawczo techniką ICP OES i dokonano oceny statystycznej otrzymanych wyników. Poziom stężenia glinu labilnego w wodach: 26–34 $\mu\text{g}/\text{dm}^3$ oraz glinu wymiennego i kwasowego w osadach: 5–34 mg/g nie wskazuje na zagrożenie dla hodowli ryb pod warunkiem, że zachowana będzie kwasowość wody. Przy $\text{pH} = 4,3$ następuje znaczny wzrost stężenia wszystkich oznaczanych form glinu, w tym również najbardziej toksycznego dla ryb – glinu monomerycznego nieorganicznego (Al_3), którego stężenie zwiększa się ponad 10-krotnie w porównaniu do wód o odczynie $\text{pH} = 7,1$ –8,2.