Bioaccumulation of aluminium in hydromacrophytes in Polish coastal lakes

Magdalena Senze*, Monika Kowalska-Górska

Department of Hydrobiology and Aquaculture, Wrocław University of Environmental and Life Sciences, Chelmońskiego 38C, 51-630 Wrocław, Poland, *e-mail: magdalena.senze@up.wroc.pl (corresponding author)

Abstract: The research on aluminium content was conducted in water and on aquatic flora of Polish lakes in the central part of the coast. The study included the lakes Sarbsko, Choczewskie, Białe, Kłodno, Dąbrze and Salino investigated in the summer of 2013. The examined lakes belong mainly to the direct basin of the Baltic Sea. Samples of aquatic plants and lake waters were collected. In the water samples pH and electrolytic conductivity were measured. The aluminium content was determined both in water and aquatic plants. Submerged hydromacrophyte studies included *Myriophyllum alterniflorum* L., *Potamogeton perfoliatus* L. and *Ceratophyllum demersum* L. Emergent hydromacrophyte studies included *Phragmites australis* (Cav.) Trin. ex Steud., *Juncus bulbosus* L., *Iris pseudacorus* L., *Eleocharis palustris* (L.) Roem.&Schult., *Phalaris arundinacea* L., *Carex riparia* Curt., *Mentha aquatic* L., *Stratiotes aloides* L., *Alisma plantago-aquatica* L., *Glyceria maxima* (Hartman) Holmb., *Sagittaria sagittifolia* L., *Scirpus lacustris* L. and *Typha angustifolia* L. The purpose of this investigation was the determination of the aluminium content in submerged and emergent hydromacrophytes and also the definition of their bioaccumulative abilities. The average concentration of aluminium in water was $2.68 \mu\text{g Al dm}^{-3}$. The average content of aluminium in plants was $2.8015 \text{ mg Al kg}^{-1}$. The bioaccumulation factor ranged from $\text{BCF}=19.74$ to $\text{BCF}=16619$. On the basis of the analysis of the aluminium content in water and aquatic plants results show that both water and plants were characterized by a moderate level of aluminium. The recorded concentrations indicate a mid-range value and are much lower than those which are quoted for a variety of surface waters in various parts of the world.

Key words: aluminium, water, lake, bioaccumulation, aquatic plants

Introduction

Aluminium is one of the primary components of the earth's crust. It occupies the third position after oxygen and silicon. Its amount in rocks depends on the type of rock material. In igneous and clayey rocks it makes up the highest quantity and its average content reaches 8%. Aluminium predominantly occurs in compounds in trivalent form and has an affinity to oxygen bonds. During weathering hydroxides with a different valency from $\text{Al}(\text{OH})^{2+}$ to $\text{Al}(\text{OH})_6^{3-}$ are created. The amount of aluminium in the atmosphere is related to dust. It is the only component which does not succumb to enrichment in atmospheric dust in proportion to the crust's composition. That is why it is also used to estimate relative changes in the concentration of other elements. Above populated areas the level of aluminium in the air increases. Hence, over

the northern hemisphere the content of aluminium is about ten times greater (120 ng m^{-3}) than in the southern hemisphere (12 ng m^{-3}). In man's direct surrounding aluminium is present in drugs, cosmetics or as addendum in edible products. It is used to manufacture light alloy for electrical conductors, chemical equipment, to produce sheets, foil, dishes and kitchen utensils. A natural source of aluminium for people is water percolating in acidic rocks and soils and polluted water pipes (Borkowska 1988; Kabata-Pendias and Pendias 1999; Barabasz et al. 2002; Gworek 2006).

In plants aluminium commonly occurs. Aluminium content in plants varies and depends on the plant's characteristics and soil conditions. Plants growing on an acidic soil gather a higher amount of oxygen. The excess of aluminium in plants unfavourably affects them, which is the cause of disturbances in the uptake and transport of nutrients, and has adverse

effects on cell membranes, cell division and DNA synthesis. Known sensitivity of certain plant roots to an increase in the amount of mobile aluminium is used for bioindicative purposes. Aluminium creates comprehensive hydrated forms and polycyclic compounds in water. Its level in surface waters is quite low, because the solubility of aluminium in water depends on the acidity and most surface waters do not have adequate acidity to dissolve aluminium. Aluminium's solubility increases in a solution that has a pH<6.0 or pH>8.0. Aluminium is easily absorbed by sediments in the form of metastable compounds and may be launched as the water's acidification increases. Aluminium accumulates in the food chain in the aquatic environment. Aluminium's harmful action triggers its precipitation on fish's gills and its greatest amount is noticed in marine organisms' hard tissues (Borkowska 1988; Severi 1997; Kabata-Pendias and Pendias 1999; Barabasz et al. 2002; Wauer et al. 2004; Gworek 2006; Oberholster et al. 2012).

Accumulation of metals in water plants is very diverse and dependent on many factors. For example, the type of reservoir, plant species, the level of pollution, and the elapsed time of exposure to contamination are crucial (Kabata-Pendias 1999). It may be expected that when the concentration of metals in water rises, their amount in plants will increase. It is also proven that exposure to low concentrations over a long period of time favours the accumulation of larger amounts of metals in plant tissues (Borkowska 1988; Severi 1997; Kabata-Pendias and Pendias 1999; Barabasz et al. 2002; Wauer et al. 2004; Gworek 2006; Oberholster et al. 2012).

Within lakes submerged and emergent plant species occur. They mainly overgrow the littoral zone – the strip/part of the reservoir with a relatively easy accessibility to the researcher. It is predominantly in this zone that the highest number of plants occurs whose acquisition is not a problem and whose bioaccumulative abilities may become useful to define the quality of the aquatic environment. The purpose of this investigation was the determination of the aluminium content in submerged and emergent hydromacrophytes and also the definition of their bioaccumulative abilities.

Methods

The research material was water and plants from coastal lakes. Samples were collected in July and

August 2013. Each time three samples of water were collected from the littoral zone, together with the acquired hydromacrophytes. On-site pH reaction (PKN 1990) and electrolytic conductivity of water (PKN 1999) were determined.

Water samples were collected by a boxcorer for polyethylene bottles (PKN 2003). The water was filtered on 0.45 Whatman 1 filters. To mineralize aluminium in water the samples were treated with concentrated HNO₃ (measuring procedure – PB-10/I, VARIAN - developed analytical methods).

The following species of aquatic plants from submerged hydromacrophytes were collected: *Myriophyllum alterniflorum* L., *Potamogeton perfoliatus* L. and *Ceratophyllum demersum* L. Among the emergent hydrophytes the following were collected: *Phragmites australis* (Cav.) Trin. ex Steud., *Juncus bulbosus* L., *Iris pseudacorus* L., *Eleocharis palustris* (L.) Roem.&Schult., *Phalaris arundinacea* L., *Carex riparia* Curt., *Mentha aquatic* L., *Stratiotes aloides* L., *Alisma plantago-aquatica* L., *Glyceria maxima* (Hartman) Holmb., *Sagittaria sagittifolia* L., *Scirpus lacustris* L. and *Typha angustifolia* L. (PKN 2006). In total 25 species of plants were collected.

Plants were washed several times with water from the lake to remove impurities, then rinsed three times in redistilled water and dried at room temperature (22°C) until dry. Samples were cut, ground and homogenized. 0.5 g of each sample was transferred to a teflon vessel HP-500 and mineralized in a microwave oven Mars 5 CEM with concentrated HNO₃ using a three-step mineralization. After cooling to room temperature the supernatants was transferred to serological tubes and diluted with redistilled water to 25 cm³.

Designations of the content of aluminium in the samples were made by atomic absorption spectrophotometry Spectra AA-110/220 Varian (PKN 1992). The detection limit is 0.0001 mg dm⁻³.

The aluminium's bioaccumulation factor was specified (BCF) as the ratio of aluminium content in plants to the amount of metal in water (Jezierska and Witeska 2001):

$$BCF = C_p / C_w$$

where: BCF is the bioaccumulation factor, C_p is the metal concentration in the plant, and C_w the metal concentration in the water.

Analysis of the results was performed in Microsoft Office Excel 2003 and Statistica 10.

Fig. 1. Location of sampled lakes

Table 1. Morphometric characteristics of coastal lakes (Jańczak 1997)

Morphometric indicator	Białe next to Chmielno	Choczewskie (Choczewo)	Dąbrze	Salińskie (Salino)	Kłodno	Sarbsko
Latitude [ddmm.m]	54°20.1'	54°44.2'	54°39.4'	54°40.8'	54°19.3'	54°45.0'
Longitude [ddmm.m]	18°06.9'	17°55.8'	17°57.8'	17°55.8'	18°06.6'	17°37.6'
Altitude [m a.s.l.]	160.6	44.0	106.0	91.0	160.5	0.5
Surface [ha]	96.3	177.7	57.6	70.7	128.1	651.7
Volume [dam ³]	7535.3	6345.3	1680.7	2250.0	14123.0	8074.2
Maximum depth [m]	21.6	12.9	5.6	8.6	38.5	3.2
Average depth [m]	7.8	3.6	2.9	3.1	11.0	1.2
Maximum length [m]	1550	2350	1140	2400	2070	6580
Maximum width [m]	850	1380	860	800	940	1240
Shoreline length [m]	4725	6525	3235	6300	6050	15500
Shoreline development	1.36	1.38	1.20	2.11	1.51	1.71
Unveiling's indicator	12.3	49.4	19.9	22.8	11.6	543.1

Study area

For the study, six lakes located in the northern part of Poland were chosen (Fig. 1). The lakes are located in the catchments of the Pomeranian rivers Łeba (Lake Sarbsko) and Piaśnica (Lakes Choczewskie, Dąbrze and Salińskie), as well as in the catchment of the River Radunia, a third order tributary of the River Vistula (Lakes Białe and Kłodno). Four of them are covered with a programme of environmental monitoring conducted by the Regional Inspectorate of Environment Protection (RIEP). This monitoring is carried out within the framework of the national monitoring network and those lakes belong to the group of benchmark lakes.

Lakes Białe, Choczewskie, Dąbrze and Salińskie belong to areas with a low degree of human impact on the environment. Only Lakes Sarbsko and Kłodno are subject to a strong impact of anthropogenic pollution. The lakes are situated in the catchment areas of forest and agro-forest. In the area there are no point sources of pollution. Morphometric characteristics of the lakes studied are presented in Table 1.

Results and discussion

The pH of the water tested was in the very wide range of values from acidic to basic. The lowest pH values were measured in Lakes Dąbrze (average pH 4.66) and Salino (average pH 5.04) and the highest in Lake Sarbsko (average pH 9.14) (Table 2). Only the water of Lakes Choczewskie and Białe had a pH close to neutral, allowing its classification as Class I purity of surface water (pH 6.00-8.50) in accordance with the standards of the Regulation of the Minister of the Environment from 9 November 2011 regarding the classification of the status of surface waters.

Table 2. Water reaction (pH) and electrolytic conductivity ($\mu\text{S cm}^{-1}$) in water of coastal lakes (mean values)

Lake	Water reaction	Electrolytic conductivity
	[pH]	[$\mu\text{S cm}^{-1}$]
Białe	7.86	291.00
Choczewskie	7.43	141.50
Dąbrze	4.66	46.50
Salino	5.04	34.60
Sarbsko	9.14	353.00
Kłodno	7.85	195.63

The water of the examined lakes was estimated as weakly mineralized. Electrolytic conductivity is maintained at a level of $46.50 \mu\text{S cm}^{-1}$ (mean value) in Lake Dąbrze to $353.00 \mu\text{S cm}^{-1}$ (mean value) in Lake Sarbsko (Table 2). The conductivity was therefore typical for lowland waters with low and medium pollution. These lakes (not counting Sarbsko and Kłodno) are selected as monitoring lakes covered by the national network, characterized by low human pressure. A higher electrolytic conductivity compared with other lakes was measured in Lake Sarbsko, which is most likely the result of the influence of tourist activity. In the catchment area of this lake, in contrast to the other studied water bodies, a number of tourist base facilities are located. Additionally the increased conductivity may be engendered by a so-called tidal bore, injecting saline water from the Baltic Sea. The overall picture of conductivity tested in the lakes according to the Regulation of the Minister of the Environment of 9 November 2011 (on the classification of the status of surface water of studied lakes) shows that the lakes are classified at the level of Class I (MŚRP 2011).

The concentration of aluminium in the water of the examined lakes ranged from $1.10 \mu\text{g Al dm}^{-3}$ (Lake Kłodno) to $6.80 \mu\text{g Al dm}^{-3}$ (Lake Salino) (Table 3). Increased levels of aluminium in the lakes are observed as follows: Kłodno < Dąbrze < Białe < Choczewskie < Sarbsko < Salino. According to the Regulation of the Minister of the Environment the aluminium concentration in lake waters is low, below the limit of being harmful to the aquatic environment ($\leq 0.4 \text{ mg Al dm}^{-3}$) and is therefore classified as first class.

Looking at the other examined reservoirs located in the coastal area of northern Poland the detected concentrations are extremely low. The values presented by Kubiak et al. (2013) for the water of lakes located in the region of Western Pomerania, and whose catchment area is not particularly dirty, seem high ($18.00\text{--}80.00 \mu\text{g Al dm}^{-3}$). Also the lakes studied in the area of the National Park and protected Ukrainian lakes (national park) are characterized by a similar level presented by Sobczyński and Joniak, 2009, Linnik et al. 2012 and Kubiak et al. 2013.

As in the reservoirs with protected catchments without strong contamination higher concentrations of aluminium are found than in lakes of Pomerania, it can be expected that in surface waters subjected to strong anthropogenic impact even higher concentrations of aluminium may occur. This is confirmed by the results of many water bodies in and outside Po-

Table 3. Aluminium content in aquatic plants (mg Al kg⁻¹d.w.), aluminium concentration in lake water (µg Al dm⁻³), and bioaccumulation factor (BCF) in lakes

Lake	Plant species	Plants	BCF	Water
			min-max x±SD	
Lake Białe	<i>Phragmites australis</i> (Cav.) Trin. ex Steud.	0.53-3.79 2.18±1.22	359.86-2530.40 1454.78±818.57	1.30-1.70 1.50±0.20
Lake Dąbrze	<i>Juncus bulbosus</i> L.	2.62-3.52 3.07±0.63	1875.14-2515.14 2195.21±452.64	1.20-1.60 1.40±0.20
Lake Choczewskie	<i>Phragmites australis</i> (Cav.) Trin. ex Steud.	0.05-0.08 0.06±0.01	35.43-51.93 42.56±7.68	1.40-1.80 1.60±0.20
	<i>Juncus bulbosus</i> L.	0.26-0.31 0.28±0.04	162.50-199.13 180.81±25.89	
	<i>Iris pseudacorus</i> L.	0.35-0.45 0.40±0.06	223.31-282.56 252.93±41.98	
	<i>Eleocharis palustris</i> (L.) Roem.&Schult.)	0.29-0.37 0.33±0.05	187.12-234.87 211±33.76	
	<i>Phalaris arundinacea</i> L.	0.13-1.27 0.51±0.53	19.74-193.48 77.71±80.48	
Lake Salino	<i>Carex riparia</i> Curt.	0.31-0.38 0.34±0.52	47.15-58.30 52.72±7.88	6.40-6.80 6.60±0.20
	<i>Phragmites australis</i> (Cav.) Trin. ex Steud.	0.06-1.47 0.72±0.43	38.81-777.84 391.34±233.55	
	<i>Juncus bulbosus</i> L.	0.78-2.13 1.54±0.59	488.12-1335.06 964.65±373.39	
Lake Sarbsko	<i>Mentha aquatic</i> L.	0.34-11.29 4.18±6.16	172.45-5645.15 2091.23±3081.05	1.50-6.60 3.80±2.00
	<i>Stratiotes aloides</i> L.	3.75-5.14 4.44±0.97	1977.57-2706.31 2341.94±515.29	
	<i>Potamogeton perfoliatus</i> L.	5.00-5.04 5.02±0.03	2969.05-3127.68 3048.37±112.16	
	<i>Myriophyllum alterniflorum</i> L.	13.24-15.52 14.38±1.60	6624.05-7760.70 7192.37±803.73	
	<i>Alisma plantago-aquatica</i> L.	0.39-0.55 0.47±0.11	199.65-278.15 238.90±55.51	
	<i>Ceratophyllum demersum</i> L.	4.72-12.83 6.89±2.45	927.83-7548.17 4031.50±2394.93	
	<i>Glyceria maxima</i> (Hartman) Holmb.	0.42-0.45 0.44±0.01	214.45-226.95 220.70±8.83	
	<i>Carex riparia</i> Curt.	0.42-33.23 11.89±15.16	214.75-16619.95 5946.56±7581.14	
	<i>Sagittaria sagittifolia</i> L.	7.98-8.53 8.26±0.38	4202.84-4493.11 4347.97±205.25	
	<i>Scirpus lacustris</i> L.	0.66-1.58 1.06±0.42	331.15-835.15 548.15±233.51	
	<i>Typha angustifolia</i> L.	0.25-0.36 0.31±0.08	169.40-243.93 206.66±52.70	
	<i>Phragmites australis</i> (Cav.) Trin. ex Steud.	0.33-2.50 0.92±1.05	255.53-1925.76 713.86±809.13	
	<i>Ceratophyllum demersum</i> L.	4.98-5.43 5.20±0.31	3835.07-4177.00 4006.03±241.78	
	<i>Carex riparia</i> Curt.	0.19-0.23 0.21±0.02	152.61-182.07 167.34±20.83	
	<i>Typha angustifolia</i> L.	0.04-0.12 0.07±0.04	33.00-97.92 61.00±33.36	
Lake Kłodno				1.10-1.30 1.20±0.08

land regardless of whether waters are static or flowing (Sorenson et al. 1974; Kovác et al. 1985; Rodushkin et al. 1995; Neal et al. 2000; Järvinen et al. 2002; Jordão et al. 2002; Kozubek and Marek 2002; Guibaud et al. 2003; Samecka-Cymerman and Kempers 2003; Samecka-Cymerman and Kempers 2004; Bojakowska et al. 2010; Gunkel et al. 2011; Senze et al. 2011; Biel and Piaseczna 2012; Selvam et al. 2012; Senze and Kowalska-Górska 2013).

A significant impact on the level of aluminium in water is their pH reaction. The more acidic the pH the more the concentration of aluminium in water is increased (Sprenger and McIntosh 1989; McKnight and Bencala 1990; Wrobel 1993; Vesely et al. 1998; Reitzel et al. 2013). The coastal lakes Dąbrze and Salino were characterized by acidic water and there we could expect a higher concentration of aluminium in water. However, higher values were observed only in Lake Salino. Is such a dependence typical for this aquatic environment? Maybe year-long studies of those water bodies would bring new light to this issue.

The content of aluminium in aquatic flora that occurs in water bodies with static and flowing water shows a very wide range and depends on many environmental factors and plant species. The composition of the substrate and water from which the flora derives nutrients has a high impact. The range of concentrations of aluminium in water plants ranged between $0.04 \text{ mg Al kg}^{-1}$ and $33.24 \text{ mg Al kg}^{-1}$ (Table 3). The lowest value was recorded in the narrowleaf cattail collected from Lake Kłodno and the highest in the greater pond sedge collected from Lake Sarbsko. Among the collected aquatic plants were both submerged and emergent representatives. As expected it was found that the submerged plants accumulated more aluminium than representatives of the emergent plants. For the submerged group the average content of aluminium was $6.71 \text{ mg Al kg}^{-1}$ ranging from $1.77 \text{ mg Al kg}^{-1}$ to $13.25 \text{ mg Al kg}^{-1}$. On the other hand emergent plants had a value range between $0.04 \text{ mg Al kg}^{-1}$ and $33.24 \text{ mg Al kg}^{-1}$, but the mean value was lower than in the submerged plants – $2.04 \text{ mg Al kg}^{-1}$.

The values observed in the present study are, however, relatively low, compared to those reported in the literature for submergent and emergent aquatic plants (Samecka-Cymerman and Kempers 2001, 2003, 2004; Senze and Kowalska-Górska, 2013).

Bioaccumulation of aluminium in aquatic plants expressed as the bioaccumulation coefficient ranged from $\text{BCF}=19.74$ to $\text{BCF}=16619$ (Table 3). The

minimum value occurred in reed canarygrass from Lake Salino, with a maximum in the greater pond sedge collected from Lake Sarbsko.

The overall picture of the value of the factor of aluminium's bioaccumulation of submerged and emergent plant species points to the advantage of the first group. This is evidenced by the mean values, which were as follows: $\text{BCF}=3849.7$ and $\text{BCF}=1143.0$. The range for emergent hydromacrophytes ranged from $\text{BCF}=19.74$ to $\text{BCF}=1661.9$ (Table 3). For submerged plants this range was between $\text{BCF}=927.83$, and $\text{BCF}=7548.1$ (Table 3). Not for all lakes, however, can this relationship be established. In Lakes Białe, Dąbrze and Salino only representatives of one or two species were collected. It is therefore difficult to conclude and compare the ability of bioaccumulation between groups of submerged and emergent plants. However, such a comparison can be made within the samples obtained from Lakes Sarbsko, Kłodno and Choczewskie, where a dependency could be noticed between a greater bioaccumulation in submerged rather than in emergent plants.

The presented bioaccumulation factor values calculated for coastal lakes can be found in similar ranges, as presented for water bodies located in Poland and abroad (Samecka-Cymerman and Kempers 2003; Samecka-Cymerman and Kempers 2004; Senze and Kowalska-Górska 2013). A bioaccumulation range of coastal lakes can also be arranged in the following manner: Salino < Choczewskie < Sarbsko < Kłodno < Białe < Dąbrze. But does it reflect fully the conditions and bioaccumulative dependency of submerged and emergent plants if not all lakes were contaminated on the same level as Lake Sarbsko? Chemical analyses of sediments, not conducted in the present stage of research, would contribute in the future to a better understanding of the aluminium-plant relationships. Certainly the continuation of research in this coastal area would be justified.

Conclusions

The concentration of aluminium in coastal lakes remained at a moderate level. The pH of water varied from acidic to alkaline. The level of aluminium in aquatic plants was relatively low and typical for environments subject to poor human pressure.

Bioaccumulation of aluminium in flora was typical for water bodies with a low level of contamination. The level of aluminium as found in the water

of lakes and hydromacrophytes is such that the hazard to the aquatic environment of lakes can be qualified as low.

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