

A Speciation Analysis of Aluminium in the River Silnica

E. Bezak-Mazur, M. Widłak*, T. Ciupa**

Technical University of Kielce, Department of Water and Sewage Treatment, Aleja 1000-lecia 7, 25-314, Kielce, Poland

*Group of Society School, Kielce

** Poland Pedagogical University of Kielce, Institute of Geography

Received: November 11, 2000

Accepted: March 9, 2001

Abstract

This paper presents the results of speciation analysis of aluminium in the River Silnica. The concentration of individual aluminium forms has been correlated with the select physical and chemical parameters of water.

Keywords: aluminium determination, speciation analysis

Introduction

Aluminium is a very common component of the lithosphere, and part of aluminosilicates, and is insoluble in water under normal conditions. Its solubility considerably increases as a result of acidifying caused by acid rain; an increase in solubility is especially significant when weakly buffered soils are involved [1, 2].

There are two ways that aluminium gets into surface waters:

1) alongside waste water (from plants producing aluminium and its salts or making use of it in their production);

2) by leaching from minerals containing this element in the form of different aluminosilicates. Low pH value (<4.2) favour the process of hydrolytic aluminium weathering from minerals in the form of $[Al(H_2O)_6]^{3+}$ ion [3, 4]. Processes of water conditioning where aluminium compounds act as coagulants are another source of aluminium; as such the following are used: initially hydrolyzed aluminium chlorides under the trademarks PAC, PAX as well as ALF (a mixture of aluminium salt and iron) [5-7].

The value of pH affecting the hydrolysis of aluminium ions is the most crucial factor that accounts for the form of aluminium occurrence [8, 9]. In acid waters where pH

is less than five (pH <5) aluminium occurs as a simple $[Al(H_2O)_6]^{3+}$ ion. With an increase in pH of water caused by, for example, anthropogenic factors, hydrocomplex ions $[Al(H_2O)_5(OH)]^{2+}$, $[Al(H_2O)_4(OH)_2]^+$ appear. Within the pH range of 4.5 - 5.5 $[Al(H_2O)_6]^{3+}$ ions form numerous complex combinations with ligands present in water - organic and inorganic impurities, for example, with humus acids and fluorides [10-12]. Both combinations can be subject to polymerization and multimolecular structures. Within pH ~ 6.0 a slightly soluble $Al(OH)_3$ begins to occur, and from pH = 6.2 on there are much more soluble ionic forms of the type: $[Al(H_2O)_2(OH)_4]^-$, $[Al(H_2O)(OH)_5]^{2-}$. A change in solubility accompanying changes of chemical forms results in very differentiated concentrations of aluminium taking on values ranging between 0.001 and 1.0 mg/dm³ in waters of neutral and slightly alkaline reactions, and in acid waters even up to 100 mg/dm³ [13, 14]. The best conditions of absorbing aluminium are observed at pH ~4.0 where the $[Al(H_2O)_6]^{3+}$ ion is found. This ion and hydrolytic forms $[Al(OH)]^{2+}$, $[Al(OH)_2]^+$ are considered toxic [15, 16]. The influence of aluminium upon plants depends on its concentration in the soil solution and on the efficiency of the biochemical immunity mechanism of a plant. The phytotoxic effect of aluminium manifests itself in disturbances of root growth, in the disappearance of capillaries, in brown growing points of roots, in reduced dry substance of green parts, in shedding of leaves and in wither-

Table 1. The present quality standards of waters.

1.	Recommendations for potable water: – Order of Ministry of Health, 2000 – value recommended by the EU – maximum value by the EU – standard in Germany, France, Finland – standard in Sweden – WHO	0.20 mg/dm ³ 0.05 mg/dm ³ 0.20 mg/dm ³ 0.20 mg/dm ³ 0.10 mg/dm ³ 0.20 mg/dm ³
2.	Permissible concentration in industrial waste waters entering municipal sewage systems – Order of the Cabinet, Government Regulations and Laws Gazette, May 19, 1999, Item 501 – Indices of pollution of inland surface	3.0 mg/dm ³ non-standardized
3.	Quality classification of plain underground waters for monitoring Government Regulations and Laws Gazette, 1991; amendments, 1995 Water class: Ia Ib II III	0.10 mg/dm ³ 0.20 mg/dm ³ 0.20 mg/dm ³ 0.25 mg/dm ³

ing [16, 17, 18]. A degenerated root system is incapable of sufficient amounts of water and mineral components.

Aluminium often substitutes iron and magnesium in mammals (people), and its excess results in disturbances of metabolic processes. This metal also takes the place of calcium in bones [19]. Besides, aluminium is likely to be responsible for Alzheimer's disease, disseminated sclerosis, parkinsonism, epilepsy, some neoplasms, and Down's syndrome [20-24].

Aluminium in its ionic form is toxic to most organisms living in water such as seaweeds, crawfish, and fish. At high concentrations of aluminium gills get clogged with colloidal forms of hydroxoaluminium complexes, whereas at lower concentrations the permeability of epithelium in fish-gills increases, which results in the loss of osmoregulation equilibrium of an organism [25]. More complex forms, polimeric, are not practically absorbend by living organisms. Therefore, while analysing the abundance of aluminium in surface waters it is very useful to make a speciation analysis which makes it possible to determine simple and polimeric forms, and the content of toxic forms in particular. Unfortunately, the existing quality standards of waters determine the total value of aluminium only, but not in all cases (Table 1).

Materials and Methods

The present investigations aimed at making a speciation analysis of aluminium in the water of the River Silnica with special reference to toxic forms.

The River Silnica is 17 kms long. It begins in the southeastern part of the Wilkow valley and flows through the woodland and the town. In view of the fact that there is neither a separate sewage system of rain water nor a rain water treatment plant, the Silnica is a receiver of the waters flowing down from the areas of compact settlement, from streets, market places and different industrial establishments. All polluted waters are directed into the river via interceptors and drains. There are 15 interceptors and about 80 drains throughout the river,

including 52 drains within the town. According to the studies made by the Institute of Geography in the Pedagogical University of Kielce, Poland, pollutant loads of impurities entering the river in this way are considerable [26] (Table 2).

Table 2. Loads of pollutants in raw rain sewage from the Silnica basin [26].

Type of pollutants	Quantity of impurities
Suspended matter	3 728 284.0 kg/year
ChZT _{Cr}	1 373 722.0 kg O ₂ /dm ³
BZT ₅	361 364.0 kg O ₂ /dm ³

Considering the strong anthropopression affecting the waters of the Silnica, it seemed advisable to analyse the effect of changeable physical and chemical parameters of its waters on the forms of aluminium occurrence in the context of their changeable toxicity. Samples of water under analysis were taken throughout the year at 6 sites (see map Fig. 1).

Experimental

Samples of water under analysis were taken into polyethylene containers washed with nitric acid (V) and rinsed with doubly distilled water. In the samples pH was determined according to polish standard PN-74/C-04540/01, suspended matter according to PN-78/C-04559/02, phosphates (V) to PN-91/C-04537/06, nitrates (V) to PN-82/C-04576/08. To determine aluminium, the spectrophotometric method described in PN-92/C-04605/02 was used; it consisted of the reaction of aluminium ions and eriochromocyanine R at pH = 6.1 ± 0.1 with the formation of pink and red complex compound with the maximum of absorption at 535 nm.

The investigations of aluminium speciation made use of Driscoll's method [27], whose version without sample acid pulping promotes direct measurement of two fractions:

- of total monomeric aluminium Al_{tm}
- of non-labile monomeric aluminium Al_{nl} being determined upon a sample passing through a column with Amberlit.

The difference between $Al_{tm} - Al_{nl} = Al_{nm}$ makes it possible to measure indirectly the content of monomeric inorganic aluminium, i.e. the toxic fraction containing aluminium as an Al^{3+} ion, of simple hydrolytic forms $[Al(OH)]^{2+}$, $[Al(OH)_2]^+$, of fluorides, sulphates, etc. [27, 28].

To avoid releasing aluminium from organic compounds during ion exchange, which results in overstating the results of the fractions, the "monomeric inorganic aluminium" resin was initially conditioned with the solution of NaCl. According to Berggren [29] the conditioning of local samples whose changeable content of organic compounds is expressed by the content of total organic carbon is justifiable.

Besides, the selection of Driscoll's method was justifiable as it makes analyzing of aluminium easy. The forms of aluminium separated by this method quickly react with eriochromocyanine R [27] and can be determined by the simple spectrophotometric method.

According to Driscoll's [27, 30] procedure and its modification by Backes and Tipping [31], Amberlite IR-120 was used as cation exchange resin. The length of the ion exchange column was 15 cm, bed volume was 10 ml, the flow rate was 4 ml/min. Before ion exchange the resin was conditioned by NaCl. The volume of 60 ml 1×10^{-4} m NaCl was used for conditioning purposes.

Reagents of recognized analytical quality and doubly distilled water were used in the investigations. Standard solutions of aluminium were prepared with the use of the standard by MERCK.

Results and Discussion

Table 3 shows exemplary results of analyses made from samples taken throughout the profile of the river within a single day.

Considering the results of the analysis of aluminium obtained within an annual cycle, it is possible to say that the concentration of total monomeric forms (Al_{tm}) as

Table 3. Results of analysis from a day's work throughout the profile of the River Silnica 11.01.99 (n=3).

Place of sampling (Fig. 1)	pH	mg/dm ³		
		Al_{tm}	Al_{nl}	Difference of Al_{nm}
Dąbrowa	6.25	0.12	0.08	0.04
Obwodnica	4.10	0.40	0.04	0.36
Piaski	7.72	0.04	0.04	0.0
Zalew	7.36	0.08	0.04	0.04
Pakosz	7.79	0.08	0.00	0.08
Ujście	7.71	0.04	0.04	0.00

well as that of inorganic ones ($Al_{tm} - Al_{nl}$) repeatedly exceed the admissible values of the summary content of aluminium for potable water marked as 0.2 mg/dm³ in Poland [32].

The changeability of Al concentrations was observed down the river (Table 3). There were usually recorded two maxima related to changes of pH affecting the concentration of soluble forms of aluminium. One of them was recorded at the point called "Obwodnica" and is connected with the high solubility of aluminium compounds in acid medium [8, 11]. The other maximum was recorded in the final part of the course of the river (the measuring points "Pakosz", "Ujście") where the values of pH within the range of 8.0-9.4 favour the formation of hydroxycomplexes [8, 9]. The highest values of aluminium concentrations were obtained at the measuring point "Obwodnica". Table 4 shows the values of Al_{tm} , Al_{nl} and $Al_{tm} - Al_{nl}$ for this point.

Table 4. The highest values of aluminium concentrations at the measuring point "Obwodnica" in mg/dm³.

pH	Al_{tm} ($\bar{x} \pm SD$)	Al_{nl} ($\bar{x} \pm SD$)	Difference of Al_{nm}
5.02	0.52 ± 0.04	0.08 ± 0.01	0.44
4.62	0.24 ± 0.015	0.0 ± 0.01	0.24
3.85	0.28 ± 0.015	0.0 ± 0.01	0.28
5.58	0.08 ± 0.01	nd	0.08
4.80	0.40 ± 0.05	0.08 ± 0.01	0.32
4.10	0.40 ± 0.05	0.04 ± 0.01	0.36
4.64	0.44 ± 0.05	0.04 ± 0.01	0.40
5.12	0.48 ± 0.04	0.04 ± 0.01	0.44
4.55	0.36 ± 0.05	0.08 ± 0.01	0.28
3.62 (march)	0.60 ± 0.03	0.08 ± 0.01	0.52
4.85	0.40 ± 0.05	0.04 ± 0.01	0.36
4.12	0.48 ± 0.04	0.12 ± 0.01	0.36
4.20	0.32 ± 0.05	0.08 ± 0.01	0.24
5.59	0.24 ± 0.015	nd	0.24
5.38	0.08 ± 0.01	0.04 ± 0.01	0.04
6.20	0.12 ± 0.015	0.08 ± 0.01	0.04

nd = non detected

It is to be stressed that in most analyses the concentration value of 0,135 mg/dm³ of the aluminium fraction $Al_{tm} - Al_{nl}$ considered toxic for fish [25] was exceeded here.

The data given in Table 4 show that the changeability of concentrations of individual fractions depends on the season. The above-mentioned dependence was observed by Driscoll's [27].

The results of analyses (22 analyses at 6 measuring points) obtained within a year show the high changeability of physical and chemical parameters of the Silnica observable according to both seasons and water level (fluctuations of the water level accompanying heavy rainfalls). pH values of river water samples under analysis are basically within the wide value range of 4.0-8.5.

The extreme cases were the lower of pH, namely 3.62 (springtime at "Obwodnica"), and the higher ones, namely 9.4 (June at "Pakosz"). Such annual changeability

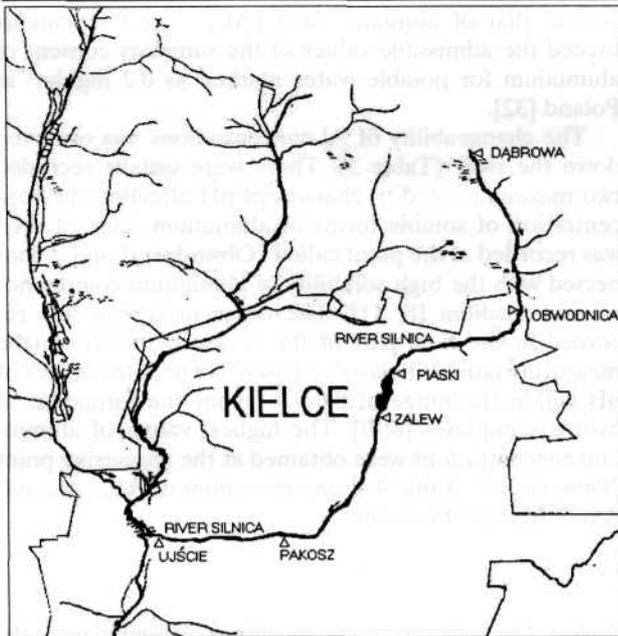


Fig. 1. Map of the River Silnica.

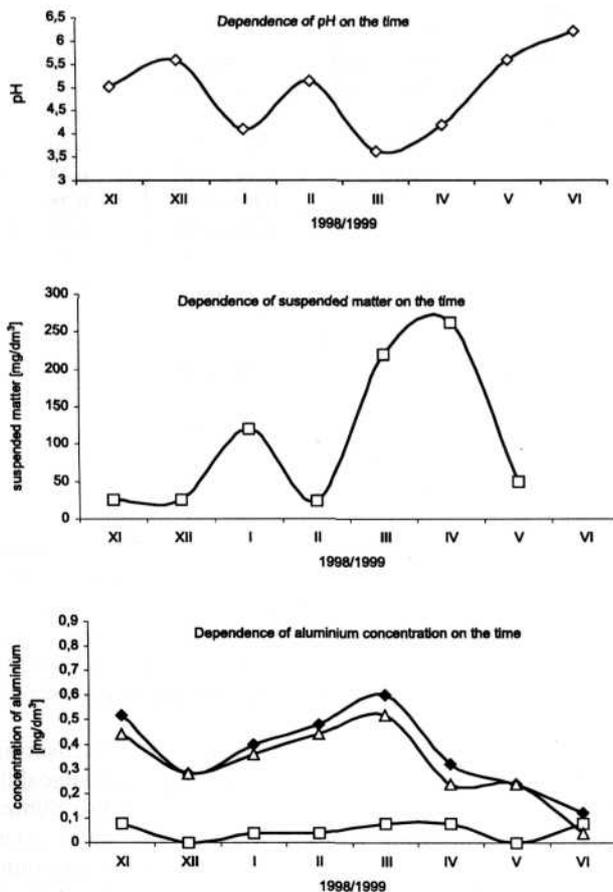


Fig. 2. Dependences of variables (pH, suspended matter, \blacklozenge cAl_{tm}/\square cAl_{nl}/Δ cAl_{nm} on the time) at the measuring point "Obwodnica" down from the River Silnica.

of pH was observed by Wrobel [3] for measuring points in the Swietokrzyskie Mountains.

For all the points low values of pH were recorded after an early spring thaw. These low values of pH are correlated with an increase in concentrations of "monomeric aluminium" (Table 4).

According to Mitrovic's [10] and Martin's [23] investigations, the contribution of the fraction containing soluble inorganic complexes of aluminium which are part of the "monomeric inorganic aluminium" fraction then increases. The dependence recorded between the "monomeric inorganic aluminium" fraction and pH proves a considerable influence of pH on the concentration of the Al_{ni} fraction [34] when waters of the high share of inorganic impurities are involved. These results caused us to investigate the content of ligands - such inorganic impurities as phosphates (V) and nitrates (V) (Fig. 3). The annual changeability of these impurities closely related to the course of the river as well as to a chosen measuring point shows the anthropogenicity of the processes taking place in the River Silnica. This is confirmed by an increase in concentration of phosphates in summer when in the presence of microorganisms the concentration should decrease [31, 33]. An increase in concentration of the Al_{nm} fraction can be accounted for by an increase in concentration of the ion $PO_4^{3-}NO_3^-$.

Considerable changes in pH were also observed down the river. At the first measuring point "Dabrowa" slightly alkaline values of pH were found, which undoubtedly resulted from woodland run-offs. The area under investigation (Tables 3 and 4, Fig. 1), which resulted from the local intense anthropogenic factors (traffic density at intersections of by-pass roads, and industrial waste from machine-shops). When the river flows through urbanized areas such as the quarter called "Pakosz" (with its leaky septic tanks and illicit sewage disposal), the reaction of water alkalizes even above 9.0. A similar annual changeability was observed in suspended matter. The highest contents of suspension treated as a measure of the content of the insoluble fraction of humus acids are shown in Figure 2.

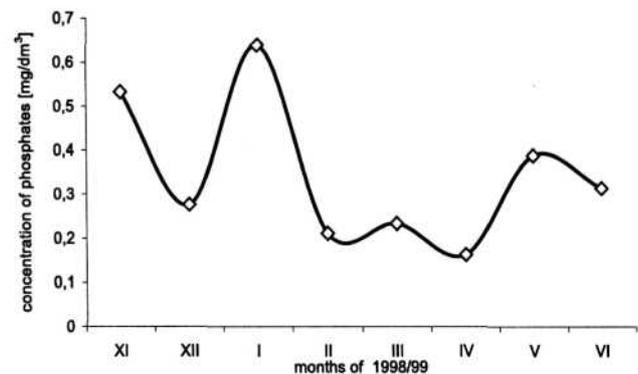


Fig. 3. Dependence of phosphates on the season at measuring point "Pakosz" down the River Silnica.

Summary

The present dependences between chemical forms of aluminium and physical and chemical parameters of water show a high variety of forms of aluminium occurrence. The concentration of the Al_{nm} fraction considered toxic was found to depend on pH, concentration of suspensions, phosphates and nitrates, which confirms the necessity of making a speciation analysis of aluminium in surface waters.

References

1. EDMUNDS W. M., KINNIBURG D. G., *J. Geol. Soc.*, **143**, 707, **1986**.
2. RAAB D, STUMM W., *Water Air Soil Pollut.*, **68**, 199, **1993**.
3. WR6BEL S., *Roczn. PZH*, **44**, 69, **1993**.
4. GRACZYK A, KONARSKI J, RADOMSKA K., DLUGASZEK M., SOBCZYNSKA J, *Glin-nowa trucizna srodowiska, Biblioteka Monitoringu Srodowiska, Warszawa*, 1992.
5. KOTOWSKI M., WIETESKA E., PAWLOWSKI L., KOZAK Z., *Charakterystyka wystepowania roznych form glinu w wybranych elementach srodowiska w Polsce, Biblioteka Monitoringu Srodowiska, Warszawa* **1994**.
6. GROCHOLSKI K, JEZ-WALKOWIAK J., SOZANSKI M., *Mat. Konf. Mikrozanieczyszczenia w srodowisku czlowieka, Czestochowa-Ustron, 8-10 wrzesnia* **1999**.
7. RAK M, SWIDERSKA-BROZ M., *Ochrona Srod*, **4**, **75**, 21, **1999**.
8. WOLBOWSKA A., ZARZYCKI R, METLEWNIAK B., *Ochrona Srod*, **4**, **75**, 25, **1999**.
9. LORGREN L., HEDLAND T, OHMAN L. O., SJOBERG S., *Wat. Res.*, **21**, 11, 1401, **1987**.
10. MITROVIC B, MILACIC R., Pihlar B, *Analyst*, **121**, 627, **1996**.
11. DRISCOLL C. T, *Inter J. Environ. Anal. Chem.*, **16**, 267, **1984**.
12. Katalog wybranych fizycznych i chemicznych wskaźników zanieczyszczeń wód podziemnych i metod ich oznaczania, t. II Biblioteka Monitoringu Srodowiska, Warszawa, **1995**.
13. KABATA-PENDIAS A, PENDIAS H., *Biogeochemia pierwiastkow sladowych*, PWN, Warszawa, **1993**.
14. MARTIN R. B., *Ace. Chem. Res.*, **27**, 204, **1994**.
15. BERGESS J., *Analyst*, **117**, 605, **1992**.
16. STARSKA K, *Roczn. PZH*, **41**, 99, **1990**.
17. BARSZCZAKT, BILSKI J, *Post. Nauk. Roln.* **3**, 21, **1983**.
18. NOWACZYK E, BORYS M., *Post. Nauk. Roln.* **6**, 3, **1974**.
19. ANDERSSON M., *Water Air Soil Pollut*, **39**, 439, **1988**.
20. GANROT P. O, *Environ. Health Perspec.* **65**, 363, **1986**.
21. KRISHNAN S. S, MCLACHLAN D.R, DALTON A. J, KRISHNAN B, A. FENTON S. S, HARRISON J. E, *Aluminium toxicity in humans, Essen, and Toxic. Trace Elem. Human Health and Dis.* Alan R. Liss, Inc., 645, **1988**.
22. HONGVE D, JOHANSEN J, *J. Trace Elements Med. Biol.*, **10**, 6, **1996**.
23. MARTIN R. M, *Bioinorganic Chemistry of Aluminium in Metal Ion in Biological Systems* M. Decker, New York, **11**, **1988**.
24. FAIRMAN B, SANZ-MENDEL A, GALLEGRO M, QINTELA M. J, JONES P, BENSON R, *Anal. Chim. Acta*, **286**, 401, **1994**.
25. WREN C. D, STEPHENSON G. L, *Environ. Pollut*, **71**, 205, **1991**.
26. Information from local government Kielce.
27. DRISCOLL C. T, BAKER J. P, BISOGNI J. J, SCHOFIELD C.L., *Nature*, **284**, 161, **1980**.
28. R. MILACIC, *Mikrochimica Acta*, **129**, 139, **1998**.
29. BERGGREN D, *Int. J. Environ. Anal. Chem.*, **35**, 401, **1994**.
30. DRISCOLL C.T, *Int. J. Environ. Anal. Chem.*, **16**, 267, **1984**.
31. BACKES C. A, TIPPING E, *Int. J. Environ. Anal. Chem.*, **30**, 135, **1987**.
32. Government Regulations and Laws Gazette, 1991, amendments, **1995**.
33. TIPPING E, BACKES C. A, *Wat. Res.*, **22**, 593, **1988**.
34. DOJLIDO J. R, *Chemia Wod Powierzchniowych, Wyd. Ekonomia i Srodowisko, Biatystok*, **1995**.
35. BENSCHOTEM A. P, *Wat. Res.* **24**, 1519, **1990**.