Letter to the Editor

Research on Aluminium Speciation in Poor Forest Soils Using the Sequential Extraction Method

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Abstract

Research on aluminium speciation was performed using a slightly modified version of Tessier's procedure. The soils under study displayed strongly acidic character (pH_{KCl} of 3.3 - 4.4). The content of aluminium in the exchangeable (11 mg/kg), acid extractable (67 mg/kg), oxidizable (2650 mg/kg), reducible (658 mg/kg) and residual fraction (24,680 mg/kg) varied widely. The percentage of labile phase (sum minus residual) obtained for mean values in the profile amounted to 12.1%, which may indicate its considerable bioavailability. The soil profile under study displayed a lithogenically dichotomous structure, which was also reflected in the aluminium content in the particular fractions.

Keywords: aluminium, soil, sequential extraction, Wielkopolski National Park.

Introduction

The growing acidification of soils has become a major environmental problem in recent years. In the second half of the 20th century many soils became much more acidified than they had over the previous few centuries [1, 2]. This process is mainly due to the emission of industrial pollution falling to the soil surface in the form of (strong) mineral acids [3, 4]. There is also internal acidification going on in the soil itself, caused by the weathering of minerals and intensive uptake of basic cations by plants. Soil acidity also results from its content of organic acids produced by the decomposition of organic matter, e.g. highly acidic fulvic acids [5, 6].

The soil is endowed with several mechanisms for counteracting this situation in the form of so-called buffering [7, 8]. Depending on soil pH, several buffers can be distinguished, such as the carbonate buffer, whose pH range (6.2-8.0), however, makes it practically irrelevant for the acid forest soils, and the buffering action of the

sorption complex (pH 4.2-5.0), whose effectiveness for these soils is also low because of their composition. The silicate buffer (pH 5.0-6.0) is important but ineffective owing to the slow pace of reactions taking place, which involve the binding of hydrogen ions through releasing alkali metals from silicate minerals. The next buffer, that of aluminium (pH 2.8-4.2), is built of aluminium compounds which release aluminium cations to the solution, thus neutralizing hydrogen ions. This process involves the decay of clay minerals via intermediate products, namely Al-hydroxy complexes of varying charge and degree of polymerization [8, 9].

Aluminium is the basic component of a majority of soil minerals; its content in Poland's soils expressed as Al_2O_3 varies from 5% to 12% [10]. The mineralogical forms of aluminium include crystalline silicates (feldspars, clay minerals), oxides and hydroxides, and microcrystalline and amorphous forms. Studies of clay minerals have shown that some of them store Al-hydroxy polymers of varying mobility in their interlayer spaces. Aluminium also forms numerous organic complexes with fulvic and humic acids that are part of the soil organic substance [11,

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12]. In undergoing the above-mentioned varieties of action, both anthropogenic and natural, the soil changes the speciation forms of elements that are its basic and trace components.

The sequential extraction of elements is a technique widely employed in environmental geochemistry [13, 14, 15] to identify those forms. The procedure rests on such a choice of extraction solvents and conditions that allow the separation of metals occurring in chemical forms that can be released to the solution under various natural environmental conditions. The first complete conception of the sequential extraction of metals, still considered fundamental, was worked out by Tessier, Campbell and Bisson [16] in 1979. Later, several other procedures were devised [14, 15, 17, 18, 19] that the European Community Bureau of Reference (BCR), now known as the Standards, Measurements and Testing Program, attempted to unify in a 5-stage process [15, 20]. The technique described is not intended to identify all chemical individuals, but it describes their types depending on the mode of binding. This kind of analysis is called fractionation and is defined by the type of chemical operations being carried out [13,15].

Over recent years much has been written on the speciation of many elements, mostly heavy metals [21, 22, 23, 24]. However, the number of studies of the speciation of aluminium, so crucial because of its toxicity [25, 26, 27] and wide distribution, still seems to be unsatisfactory. Literature contains works on the speciation of aluminium in solution [28, 29] or the speciation of soils conducted in a parallel way (not sequentially) using reagents other than BCR-recommended ones [9, 30, 31, 32].

Research on the speciation of aluminium in soils seeks to gain insight into both the current situation, i.e. forms of aluminium present at the time of study, and a probable direction of changes and transformations of aluminium complexes in the conditions of further soil acidification. It is also interesting to observe changes in the Al speciation forms down the soil profile: the formation of the eluvial horizon and its underlying illuvial horizon in which the previously leached aluminium compounds precipitate in the form of sesquioxides and organic compounds. Thus, the study of Al speciation can contribute to a better understanding of the multidirectional transformation of this element.

Results reported below supplement earlier research carried out for the same soil and concerning changes in the composition of soil solutions and the dynamics of aluminium leaching from soil monoliths under simulated conditions [33, 34]. It was found that conditions had developed where aluminium had a toxic effect on vegetation (the Ca/Al coefficient was smaller than 1, and often smaller than 0.1). Aluminium became the dominant ion (>50%) in aqueous extracts, while the amounts of aluminium eluviated from 1 m^2 of a 50-cm layer of soil during the simulation of a year's very acid precipitation varied from 1 g to 31 g [34].

The article presents the results of research on aluminium speciation in the poor forest soil of Wielkopolski National Park, discusses the proportions of individual forms with varying bioavailability, and shows their distribution in the soil profile.

Methods

Field Study

Samples were taken from the area adjacent to the Ecological Station of Adam Mickiewicz University at Jeziory situated in Wielkopolski National Park, from under a pine stand about 80 years old. Care was taken for the site of the soil profile to be located close to that from which soil monoliths had been taken for earlier research [33, 34].

After digging 1.4 m deep, samples were collected from individual genetic horizons and placed in plastic bags. Only the so-called mineral horizons were sampled, i.e. down from the A horizon of humus accumulation. Overlying it, as in any forest soil, was an organic (O) top horizon of humus commonly called litter. In the profile under study, it was discontinuous and had a negligible thickness (about 1 cm). It was removed prior to sampling the mineral horizons.

Laboratory Study

Soil samples were dried to obtain the so-called air-dry state, then crushed in a mortar and run through a 2-mm mesh sieve in order to separate skeleton particles (stones, gravel) from the fine fraction (sand, silt, clay) [35].

The following physico-chemical determinations were carried out in the <2 mm fraction:

- Granulometric analysis, using the areometric method after Casagrande modified by Prószyński (supplemented with the sieve method to fractionate sand) [35]. The particle-size classification conforms to the PN-R-04033 Polish Standard (1998) [36].
- Reaction, using a pH meter - in H_2O and 1M KCl at 1:2.5 by weight. The method consisted in measuring the pH of the suspension after 30 min. in the aqueous suspension and after 60 min. in that with the electrolyte [35].
- Organic matter, as organic C, using Tiurin's method and a mixture of 0.067M $K_2Cr_2O_7$ and concentrated H_2SO_4 in the presence of Ag_2SO_4 as catalyst. As an agent reducing the excess oxidant, use was made of 0.1M solution of Mohr's salt ($FeSO_4/(NH_4)_2SO_4 \cdot 6H_2O$) [35].

Sequential Extraction as an Analytic Speciation Technique

One of the techniques of separating the various forms of aluminium occurring in the soil is sequential extraction. It consists in the successive use of specified extraction

Table 1. Granulometric composition and classification of the analyzed samples.

Sample no.	Genetic horizon	Depth cm	Sand 2.0 -0.05 mm	Silt 0.05 -0.002 mm	Clay <0.002mm	Textural group acc. to [36]
			%			
1	A1	0 - 3	80	19	1	loamy sand
2	A2	3 - 9	77	19	2	loamy sand
3	AB	9 -18	79	16	2	loamy sand
4	B_v	18 - 42	82	15	3	loamy sand
5	C1	42 - 65	83	13	4	loamy sand
6	II C2	65 - 100	70	14	16	sandy loam
7	II C3	100 - 140	67	16	17	sandy loam

solvents and determining the aluminium content at each stage of the procedure. Tessier's method, with some modifications [37], was employed in the research described. Its detailed schematic diagram is presented in Fig. 1.

The successive stages of sequential extraction were carried out in centrifuge test tubes of 50 mL capacity. Samples were agitated in a horizontal shaker equipped with a water thermostat whose programmed temperature ranged from 20°C to 100°C with an accuracy of ±2°C. After each extraction stage the sample was centrifuged for 30 minutes. The clear solution from above the precipitate was transferred to

a calibrated polypropylene test tube with a hermetic cap. The solid remaining in the original test tube was washed with 5 mL of demineralized water, again centrifuged for 30 minutes, and combined with the first portion of the extract. Solutions from the first three extraction stages were acidified with four drops of concentrated nitric acid. Tessier's procedure was insufficient to achieve complete digestion at stage four, the so-called residual fraction. To digest the precipitate completely, a mixture of the acids $HClO_4$ and HF was used, following the technique described in [35]. Every extraction was carried three times.

The method employed for aluminium determination in all the extracts was atomic absorption spectrometry with atomization in a flame of acetylene/nitrous oxide. The spectrometer used was a Perkin Elmer A Analyst 300.

The results of the successive extractions are presented in diagrams as curves joining mid-points of a horizon's thickness.

Results and Discussion

Physico-Chemical Properties of the Soils

In terms of grain size, the soil under study displays a dichotomous structure called lithogenic discontinuity. These two parts differ substantially in their clay fractions. The particle-size distribution and classification for the particular genetic horizons are presented in Table 1. The soil profile is sandy in the upper part and loamy below 65 cm. The clay content in the loam amounts to 16-17%, as against a mere 1-4% in the top part, which is made up of loamy sand. Both the sandy and loamy parts of soil have a silt content of more than 10%.

Typologically, the soils are classed as rusty developed on glaciofluvial sands with underlying till [38]. According to the WRB classification [39] this soil belongs to Ferralic Arenosols.

Their pH and organic C content are presented in Table 2. The conducted pH determinations put them into the class of very strongly acidic soils down to the depth of
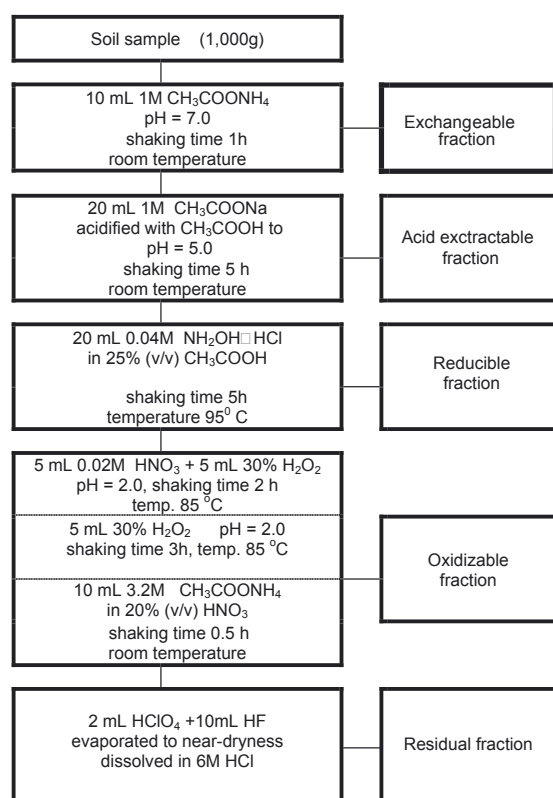

Fig. 1. Schematic diagram of the sequential extraction procedure employed.

Table 2. Reaction and content of organic matter in the analyzed samples.

Sample no.	Depth cm	C org. %	pH $_{KCl}$	pH $_{H2O}$	Classification acc. to [38]
1	0 - 3	6.9	3.2	3.8	very strongly acidic
2	3 - 9	3.6	3.3	3.8	very strongly acidic
3	9 -18	1.5	3.5	3.9	very strongly acidic
4	18 - 42	0.3	4.0	4.1	strongly acidic
5	42 - 65	0.1	4.1	4.2	strongly acidic
6	65 - 100	0.2	3.8	4.5	strongly acidic
7	100 - 140	0.2	4.4	5.2	strongly acidic

18 cm and strongly acidic further down the profile. The lowest pH (3.2) and the highest organic C content (6.9%) are characteristic of the top A horizon of humus accumulation. Further down, the pH $_{KCl}$ rises to 4.4, while organic C content drops to 0.1-0.2%.

Aluminium in the Exchangeable Fraction

The amount of aluminium ranged from about 16 mg/kg in the topsoil (A1) and the deepest parent material horizon (C3) to 5 mg/kg in horizon B$_v$ at a depth of 18-42 cm (sample no. 4). The arithmetic mean of exchangeable aluminium content in the studied profile was 10 mg/kg.

Fig. 2 presents changes in the amount of exchangeable aluminium as depth increases. The main controls of the amount of released aluminium are the amount of humus and the clay content. The concentration of weakly bound aluminium in organic humic complexes (samples no. 1-3) declines steadily with the decreasing amounts of humus (the organic C curve). In the lower soil horizons, the factor that affects the amount of exchangeable aluminium is clay content (the clay curve), because the
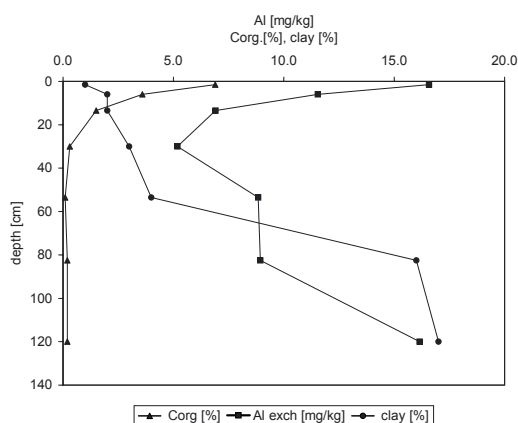
lower part of the profile contains loam deposits with a higher content of clay minerals that influences the exchange capacity.

Aluminium in the Acid Extractable Fraction

The pH of forest soils is very low due to the prolonged exposure to strong inorganic acids of anthropogenic derivation and natural organic acids. In the case under study, the top layer of the humic horizon (A1), the A2 sub-horizon and the transitional AB horizon all have a very acidic pH (pH <4.0). Hence, it is unlikely that there are any carbonates present, which usually dissolve at this stage of sequential extraction and release the co-precipitated or adsorbed ions. The use of sodium acetate in acetic acid acidified to a pH of 5.0 can release aluminium bound more tightly than in the previous extraction. The amount of aluminium in this fraction is several times greater than in the exchangeable one and varies from about 40 mg/kg in the top layer of the humic horizon (A1) and bedrock horizon (C3) to 87-97 mg/kg in samples no. 3-5. For this fraction, the arithmetic mean of aluminium content in the entire profile was 67 mg/kg. The curve depicting varia-

Fig. 2. Exchangeable aluminium in the individual horizons of the soil profile under study.
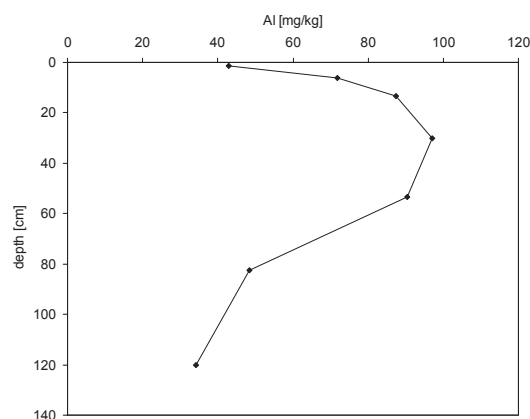

Fig. 3. Acid extractable aluminium in the individual horizons of the soil profile under study.

tions in the amount of aluminium extracted in this way is presented in Fig. 3. One can observe an increase down to the Bv horizon (18-42 cm) and then a decline accompanied by a change in the lithological character of the samples, from sand to loam.

Aluminium in the Reducible Fraction

At this stage of sequential extraction, the action of hydroxylamine hydrochloride in the environment of acetic acid and a prolonged high temperature release much greater amounts of aluminium than at the previous stages. They vary from 370 mg/kg (sample no. 1) to more than 800 mg/kg (sample no. 6); the arithmetic mean of aluminium content in this fraction was 658 mg/kg. The change in aluminium content with the depth is presented in Fig. 4. At first one can observe a steady increase (samples no. 1-3), while down from the depth of 42 cm where the parent material was found to occur there persists a similarly high concentration of about 800 mg/kg. This shape of the curve reflects the natural process of eluviation of aluminium oxides from the upper soil horizons, which stopped at a depth of roughly 42 cm.

Aluminium in the Oxidizable Fraction

The aim of this stage of sequential extraction is a nearly complete decomposition of organic matter attached to the various mineral components of the soil. The effects of hydrogen peroxide and nitric acid at an elevated temperature include not only the mineralization of organic compounds but also partial decomposition of aluminosilicates. This is indicated by very high aluminium concentrations obtained in samples nos. 1-5, amounting to nearly 2,000 mg/kg, and in the lower, loamy part of the profile, to over 4,000 mg/kg; or to 2,650 mg/kg on average. Variations in the amount of this fraction of aluminium are presented in Fig. 5. The diagram clearly indicates two lithologically different parts.
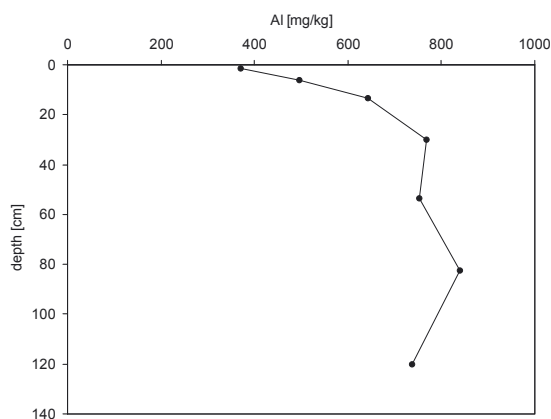
Aluminium in the Residual Fraction

As part of aluminosilicates, aluminium is one of the basic components of the residual fraction, hence its amounts are an order of magnitude larger than in the organic fraction. They are the lowest in the topmost layer, at about 18,400 mg/kg, and the highest in the lower part of the profile (sample no. 7), at 35,200 mg/kg; or 24,700mg/kg on average. Fig. 6 clearly shows a division similar to that in the oxidizable fraction: an upper part (samples no. 1-5) and a lower one (nos. 6 and 7) with much higher aluminium concentrations.

Summary

When converting the amounts of aluminium obtained at the successive stages of sequential extraction into percentages of its total amount, the following picture emerges of aluminium speciation in the soil under study (Table 3).

The smallest amounts released are those of the exchangeable form of aluminium. They constitute a few
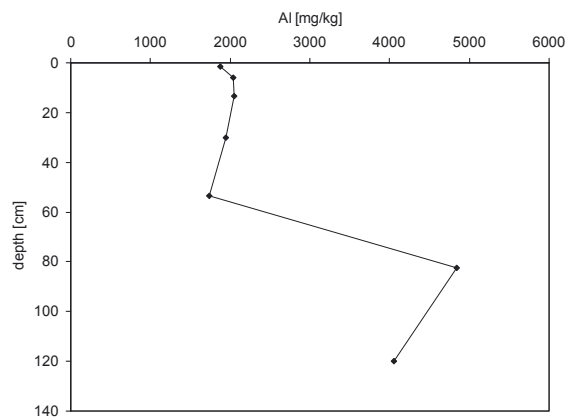
Fig. 5. Aluminium in the oxidizable fraction in the individual horizons of the soil profile under study.

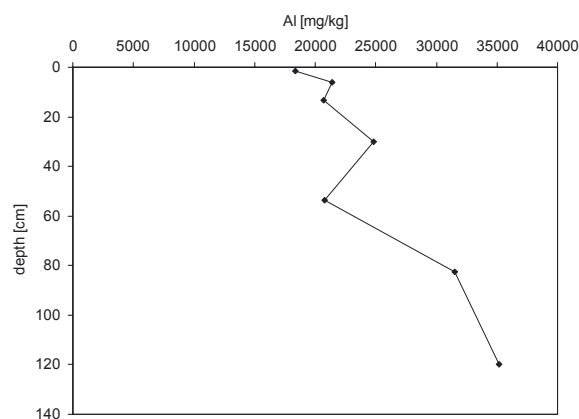Fig. 4. Aluminium in the reducible fraction in the individual horizons of the soil profile under study.

Fig. 6. Aluminium in the residual fraction in the individual horizons of the soil profile under study.

Table 3. Percentages of the particular aluminium forms obtained at the successive stages of sequential extraction of the soil profile under study.

Sample no.	Al-fraction				
	Exchangeable	Acid extractable	Reducible	Oxidizable	Residual
	%				
1	0.08	0.21	1.79	9.08	88.84
2	0.05	0.30	2.07	8.52	89.07
3	0.03	0.37	2.74	8.73	88.13
4	0.02	0.35	2.78	7.06	89.79
5	0.04	0.39	3.22	7.46	88.89
6	0.02	0.13	2.25	12.99	84.60
7	0.04	0.09	1.84	10.13	87.90

Table 4. Distribution of aluminium among the particular fractions of sequential extraction - a comparison of the results.

Fraction	Soil studied	Reference Material SRM 2710 [20]	Reference Material SRM 2711 [20]
	mg/kg	mg/kg	mg/kg
Acid extractable (exchangeable + acid extract.)	77 (10+ 67)	171	124
Reducible	658	1660	1540
Oxidizable	2650	1040	845
Residual	24,680	22,400	19,900
Labile percentage	12.1	12.8	12.6

hundredths of a percent of the total, which is equivalent to about 10 mg/kg. The acid extractable fraction of aluminium constitutes a few tens of a percent equivalent to about 67 mg/kg. Aluminium bound to iron and manganese oxides in the reducible fraction amounts to 2.5% on average, or 800 mg/kg. The highest values (apart from the residual fraction) were obtained for bound aluminium in the oxidizable fraction, considered to be the one releasing elements strongly bound to organic matter - 9% on average, or about 2,650 mg/kg.

When analyzing the percentages of the particular aluminium forms obtained at the successive stages of sequential extraction of the soil profile (Table 3), no marked differences are observed from horizon to horizon, as opposed to the absolute amounts of aluminium in the individual fractions expressed in mg/kg (see figures). The proportions of aluminium in each fraction to total aluminium content are similar irrespective of depth. The picture this comparison creates, however, does not reflect aluminium release and migration in the soil profile; these processes can be observed in the figures presented. Thus, the curves for the most readily released aluminium forms, viz. exchangeable and acid extractable (Figs. 2 and 3), assume reverse shapes: for exchangeable aluminium, horizon 4 (18-45 cm) is the one with its minimum content, while

for the acid extractable form, this is the maximum-content level. The concentrations of the acid extractable form are one order of magnitude higher, hence for total aluminium from these fractions, horizon 4 is the one in which the greatest amounts of aluminium are released. The total quantity of the element in these two fractions amounts at this depth to some 100 mg/kg, high enough to pose a threat of biotoxicity.

This regularity does not yield the expected negative correlation with the pH of the soil. Maximum pH values are recorded in the lower horizons (samples 6 and 7), and the lowest pH figures, in the three top horizons.

Aluminium concentrations in the residual fraction are very high, but the release of aluminium from aluminosilicates, which is its principal component, requires much more drastic conditions than natural. Aluminium in this fraction can be treated as a sort of background which only affects the aluminium content in the other fractions (mainly exchangeable and oxidizable).

A comparison of the results obtained with the few findings published in the literature (Table 4) must take into account slight differences in the procedures employed. There is no exchangeable fraction in the procedure proposed for the reference soil material [20]. It is contained in the acid obtained through agitating the sam-

ple with acetic acid (40 ml, 0.11M for 16 hours at room temperature). The reducible fraction differed in being acidified with 2M HNO_3 rather than with the 25% acetic acid employed here; there are also slight differences in the initial temperature when obtaining the fraction bound to organic matter. In the procedure compared, aqua regia was used for the final digestion of the sample, while in the study reported a mixture of hydrofluoric and perchloric acids was employed. The labile percentage (12.1%) obtained for the soils under analysis, i.e. the sum of all those kinds of aluminium released from fractions other than the residual, is close to that of the reference material studied by Sutherland and Tack [20]. However, the percentages of the individual fractions are different.

Conclusions

- In the successive fractions obtained using the sequential extraction method, considerable differences in aluminium concentrations were found (several orders of magnitude).
- The content of exchangeable aluminium in the soil was found to depend both on forms weakly bound to organic matter (0-18 cm) and those bound to the sorption complex of clay materials (from 65 cm down). This form of aluminium constitutes a mere 0.04% of the total.
- The content of aluminium in the acid extractable and reducible fractions (described in the literature as carbonate and bound to Fe and Mn oxides, respectively) shows a tendency to increase with depth (down to 42 cm), which can be associated with the processes of eluviation and illuviation.
- Aluminium in the oxidizable fraction, considered to be bound to organic matter, maintains the same level (down to a depth of 65 cm), to rise steeply with the change of soil type. This should be associated with aluminium present in the interlayer spaces of clay minerals rather than with the organically bound form of the element.
- The concentration of aluminium in the so-called labile forms constitutes 12.1% of its total content in the soil.
- When studying aluminium speciation in the soil using the sequential extraction method, the fraction of exchangeable aluminium should be distinguished despite its low concentrations because of its highest bioavailability, and hence possible biotoxicity.
- In order to account for all forms of aluminium, it is necessary to perchloric and hydrofluoric acids as solvents, because aqua regia does not seem to be effective enough.

References

1. TAMM C.O., HALLBACKEN L. Changes in soil acidity in two forest areas with different acid deposition 1920s to 1980s. Ambio **17**, 56, **1988**.

2. JOHNSTON A.E., GOULDING K.W.T., POULTON P.R. Soil acidification during more than 100 years uder permanent grassland and woodland at Rothamsted. Soil Use Manage. **2**, 3, **1986**.

3. GALLOWAY J.N. Acidification of the world: natural and anthropogenic. Water Air Soil Poll. **130**, 17, **2001**.

4. FILIPEK T. Natural and anthropogenic causes of soil acidification and its effects. (In Polish). Zeszyty Problemowe Postępów Nauk Rolniczych **456**, 13, **1998**.

5. POKOJSKA U. The role of humus in determination of pH, buffer properties and ion-exchange capacity of forest soil. (In Polish). Roczniki Gleboznawcze **XXXVII** (2–3), 250, **1986**.

6. PORĘBSKA G. Soil acidification and the role of aluminium in the process - a review. (In Polish). Ochrona Środowiska i Zasobów Naturalnych **9**, 102, **1996**.

7. POKOJSKA U. The forest soil resistance to acidification. (In Polish). Postępy Techniki w Leśnictwie **56**, 33, **1995**.

8. MULDER J.,VAN GRINSVEN J.J.M., VAN BREEMEN N. Impacts of acid atmospheric deposition on woodland soils in the Netherlands; III Aluminium chemistry. Soil Sci. Soc. Am. J. **51**(6), 1640, **1987**.

9. ALVAREZ E., MONTEROSSO M.L., MACROS F. Aluminium fractionation in Galician (NW Spain) forest soil as related to vegetation and parent material. Forest Ecol. Manag. **166**, 193, **2002**.

10. GLIŃSKI J. Chemical and physico-chemical properties of soil. In: B. Dobrzański, S. Zawadzki (eds.) Soil Science. (In Polish). Państwowe Wydawnictwo Rolnicze i Leśne: Warszawa, pp. 172, **1995**.

11. POKOJSKA U. Acidification of forest soil - the state of knowledge and perspectives of progress in the field. The proceedings of the conference - The natural and anthropogenic causes of soil acidification and their effects. (In Polish). Lublin, pp. 37, **1997**.

12. BERGGREN D. Speciation and mobilization of aluminium and cadmium in podzols and cambisols of S.Sweden. Water Air Soil Poll. **62**, 125, **1992**.

13. HULANICKI A. Contemporary analytical chemistry. (In Polish). Wydawnictwo Naukowe PWN: Warszawa, pp. 57, **2001**.

14. FILGUEIRAS A.V., LAVILLA I., BENDICHO C. Chemical sequential extraction for metal partitioning in environmental solid samples. J. Environ. Monitor. **4**, 823, **2002**.

15. LOPEZ-SANCHEZ J.F., SAHUQUILLO A., RAURET G., LACHICA M., BARAHONA E., GOMEZ A., URE A.M., MUNTAU H., QUEVAUVILLER PH. Extraction procedures for soil analysis. In: Quevauviller P. (ed.) Methodologies for soil and sediment fractionation studies. The Royal Society of Chemistry: Cambridge, pp. 28, **2002**.

16. RAURET G., LOPEZ-SANCHEZ J.F., SAHUQUILLO A., RUBIO R., DAVIDSON C., URE A. QUEVAUVILLER P. Improvement of the BCR three step sequential extraction procedure prior to the certification of the new sediment and soil reference materials. J. Environ. Monitor. **1**, 57, **1999**.

16. TESSIER A., CAMPBELL P.G.C., BISSON M. Sequential extraction procedure for the speciation of particulate trace metals. Anal. Chem. **51**(7), 844, **1979**.

18. SUTHERLAND R.A. Comparison between non-residual Al, Co, Cu, Fe, Mn, Ni, Pb and Zn released by tree-step sequential extraction procedure and dilute hydrochloric acid leach for soil and road deposited sediment. Appl. Geochem. **17**, 353, **2002**.

19. LO I.M.C., YANG X., Y. Removal and redistribution of metals from contaminated soils by a sequential extraction method. Waste Manage. **18**, 1, **1998**.

20. SUTHERLAND R.A., TACK F.M.G. Determination of Al, Cu, Fe, Mn, Pb and Zn in certified reference materials using the optimized BCR sequential extraction procedure. Anal. Chim. Acta **454**, 249, **2002**.

21. LENA Q.M.,GADE N.R. Heavy metals in the environment. chemical fractionation of cadmium, copper, nickel and zinc in contaminated soils. J. Environ. Qual. **26**, 259, **1997**.

22. SERIFE TOKALIOGLU, SENOL KARTAL, LATIF ELCI Determination of heavy metals and their speciation in lake sediments by flame atomic absorption spectrometry after a four stage sequential extraction procedure. Anal. Chim. Acta **413**, 33, **2000**.

23. URE A.M. QUEVAUVILLER P.,MUNTAU H., GRIEPINK B. Speciation of heavy metals in soil and sediments. An account of improvement and harmonization of extraction techniques undertaken under auspices of the BCR of the Commision of the European Communities. Int. J. Environ. An. Ch. **51**, 135, **1993**.

24. TACK F.M.G., VERLOO M.G. Single extractions versus sequential extraction for the estimation of heavy metal fractions in reduced and oxidised dredged sediments. Chem. Spec. Bioavailab. **11**, 43, **1999**.

25. POKOJSKA U. Different aspects of aluminium toxicity to plants. A review of literature from the fields of agriculture and forestry. (In Polish). XXXV, **1**, 97, **1989**.

26. HERRMANN J. Aluminium is harmful to benthic invertebrates in acidified waters but at what threshold(s). Water Air Soil Poll. **130**, 837, **2001**.

27. KOTOWSKI M., WIETESKA E., PAWŁOWSKI L., KOZAK Z. The occurrence of different species of aluminium in selected elements of the natural environment in Poland. (In Polish). Państwowa Inspekcja Ochrony Środowiska. Biblioteka Monitoringu Środowiska: Warszawa, pp. 51, **1994**.

28. BERGGREN D. The solubility of aluminium in two Swedish acidified forest soils: an evaluation of lysimeter measurements using batch titration data. Water Air Soil Poll. **114**, 137, **1999**.

29. RUSTAD L.E., FERNANDEZ I.J., FULLER R.D., DAVID M.B., NODVIN S.C., HALTERMAN W.A. Soil solution response to acidic deposition in a northern hardwood forest. Agr. Ecosyst. Environ. **47**, 117, **1993**.

30. BERGGREN D., MULDER J. The role of organic matter in controlling aluminium solubility in acidic mineral soil horizons. Geochim. Cosmochim. Ac. **59** (20), 4167, **1995**.

31. PORĘBSKA G., MULDER J. Effect of long-term nitrogen fertilization on soil aluminium chemistry. J. Ecol. Chem. **3**, 269, **1994**.

32. PELLERIN B.A., FERNANDEZ I.L., NORTON S.A., KAHL J.S. Soil aluminium distribution in the near stream zone at Bear Brook watershed in Maine. Water Air Soil Poll. **134**, 189, **2002**.

33. SIEPAK J, WALNA B., DRZYMAŁA S, Speciation forms of aluminium released under the effect of acid rain. Pol. J. Environ. Stud. **8**, 55, **1999**.

34. WALNA B., SIEPAK J., DRZYMAŁA S. Soil degradation in the Wielkopolski National Park (Poland). Water Air Soil Poll. **130**, 1727, **2001**.

35. MOCEK A., DRZYMAŁA S., MASZNER P. Genesis, analysis and classification of soils. (In Polish). Wydawnictwo Akademii Rolniczej: Poznań, pp. 416, **2000**.

36. Polish Standards, PN-R-04033. (In Polish), **1998**.

37. ZERBE J., SOBCZYŃSKI T., ELBANOWSKA H., SIEPAK J. Speciation of heavy metals in bottom sediments of lakes. Pol. J. Environ. Stud. **8** (5), 331, **1999**.

38. Collective work. Classification of forest soils in Poland, at the Information Centre of State Forests. (In Polish). Warszawa, pp. 123, **2000**.

39. World Reference Base For Soil Resources, World Soil Resources Report. FAO: Rome, pp. 84, **1998**.

40. SOBCZYNSKI T., PEŁECHATA A., ZIOŁA A., PEŁECHATY M., BURCHARDT L., SIEPAK J. Accumulation of aluminium in the freshwater ecosystem of Jarosławieckie Lake. Pol. J. Environ. Stud. **11** (Supl. I), 77, **2002**.