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FRACTIONATION OF ALUMINIUM FROM ALLUVIAL SEDIMENTS

The paper presents the results of a study on the content of aluminium in bottom sediments in the middle Odra river. A total content of this metal and the concentrations of its five species characterised by different mobility (and hence bioavailability) have been determined. Fractionation has been performed by sequential extraction according to the scheme proposed by Tessier. In the extracts, aluminium concentration has been determined by atomic absorption spectrometry. An average total content of aluminium in the sediments studied was 1.95 g/kg. The majority of the metal was permanently immobilised in the sediment and only about 1.77% of its total content was bound with the fraction released to bulk water in strongly reducing conditions.

1. INTRODUCTION

Aluminium is one of the main components of the earth crust making about 8% of its mass and is the third most abundant element after oxygen and silicon. The interest in its determination in the environment has increased from the time of discovering its adverse effect on living organisms. Its presence has also been studied in aquatic ecosystems in which aluminium in bioavailable species can pose a threat to aquatic plants and animals [1].

One of the main elements of aquatic ecosystems is bottom sediment in which the natural content of aluminium is high. This aluminium is chiefly of geochemical origin, and possible increase in its concentration due to anthropopressure is practically undetected. On the other hand, man's activity can cause significant changes in the physical and chemical conditions in bulk water leading to washing out of aluminium from bottom sediments and thus allowing it to penetrate into the food chain of the ecosystem.

The aim of the study was to assess the mobility and hence bioavailability of aluminium species from alluvial sediments from the bottom of the Odra river in its mid-

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dle section. Determination of aluminium was performed by the method of sequential extraction proposed by TESSIER et al. [2] allowing a differentiation of five fractions of this metal species. Particular stages of extraction simulated both physical and chemical conditions that can naturally occur in the near-bottom zone of the river.

2. EXPERIMENTAL

Samples of the bottom sediment to be studied were collected in June 2002 along the 75-kilometre section of the middle Odra river. The first site of sample collection was below the estuary of the Nysa Łużycka river (544 km), and the others at 544 km, 552 km, 566 km, 587 km, 670 km and 617 km below the Warta river estuary. Localisation of the sites of sample collection is shown in figure 1. The sites were in the vicinity of the cities, mainly German ones, whose municipal and industrial waste was discharged into the Odra river. The samples of bottom sediments were collected along the transversal profiles across the river bed, taking three samples from each profile: a – at a site near the river bank on the German side, b – in the mainstream, c – near the river bank on the Polish side.

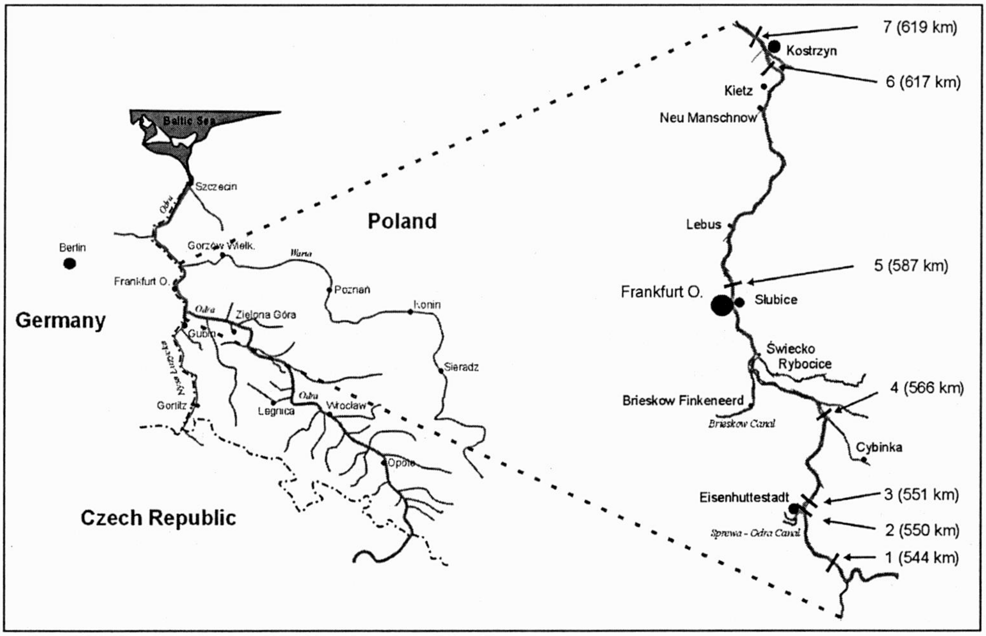

Fig. 1. Localisation of the sample collection sites

The samples were dried at 105 °C and sieved, collecting the fraction of the mesh size < 0.9 mm. Apart from the determination of aluminium, the samples were characterised by determination of the loss on ignition at 550 °C, content of organic carbon by the Tiurin method [3], content of calcium and magnesium by ASA after preliminary extraction with HCl and the content of phosphorus in an acidic extract by the molybdate method with ascorbic acid as a reducing agent [4]. The fractionation of aluminium in the bottom sediment samples was performed by sequential extraction according to the modified scheme proposed by TESSIER et al. [2]. Five fractions of aluminium species were isolated and determined.

Fraction I: Fraction of exchangeable aluminium species, the most mobile and the easiest bioavailable.

Fraction II: Aluminium bound with carbonates, released on decreasing pH of water.

Fraction III: Aluminium bound with hydrated iron and manganese oxides, released on the changes in the red-ox potential, e.g. in anaerobic conditions.

Fraction IV: Aluminium bound with organic matter, capable of dissolving or transforming into another insoluble species as a result of aerobic or anaerobic mineralisation.

Fraction V: Aluminium built into mineral structures and unavailable to living organisms.

The subsequent stages of extraction were as follows:

stage 1 – extraction with 1 M CH_3COONH_4 at pH 7 at room temperature for 1 hour,

stage 2 – extraction with 1 M CH_3COONa acidified with CH_3COOH to pH 5 at room temperature for 5 hours,

stage 3 – extraction with 0.04 M $NH_2OH{\cdot}HCl$ in 25% (v/v) CH_3COOH at 95 °C for 5 hours,

stage 4 – extraction with 0.02 M HNO_3 + 30% H_2O_2 at pH 2, at 85 °C for 5 hours, washing out with 3.2 M CH_3COONH_4 in 20% (v/v) HNO_3 for 0.5 hour at room temperature,

stage 5 – decomposition of mineral structures by HNO_3 + HF + 30% H_2O_2 for 1 hour at the boiling point.

The content of aluminium in the extracts was determined by atomic absorption spectrometry using AAnalyst 300, Perkin Elmer, with atomisation in the flame of nitrogen suboxide–acetylene.

3. RESULTS AND DISCUSSION

The samples of bottom sediments were mainly composed of coarse gravel with a small amount of organic matter. A small contribution of organic matter was confirmed by relatively small loss on ignition, of 6.3% maximum and 1.5% on average, and low content of organic carbon, of 17.3 g/kg maximum and 4.1 g/kg on average. The greatest amounts of organic matter were found in the samples collected near the river banks. The samples collected from the central part of the river bed contained little organic matter, the loss on ignition did not exceed 0.7%. The content of phosphorus was similarly low. In the samples from the site near the river bank on the German side, the maximum content of phosphorus was 2.86 g/kg (1.14 g/kg on average), in the samples collected on the Polish side it was 1.99 g/kg maximum and 0.57 g/kg on average, in a central riverbed it was 0.26 g/kg maximum and 0.21 g/kg on average. Surprisingly, much higher content of organic matter and phosphorus were detected in the samples collected on the German side, which suggested that on this side the discharge of waste was greater. The content of calcium varied from 0.06 g/kg to 2.42 g/kg (mean of 0.48 g/kg) and magnesium from 0.10 g/kg to 1.09 g/kg (mean of 0.31 g/kg). The lowest contents of calcium and magnesium were detected in the samples collected from the central riverbed.

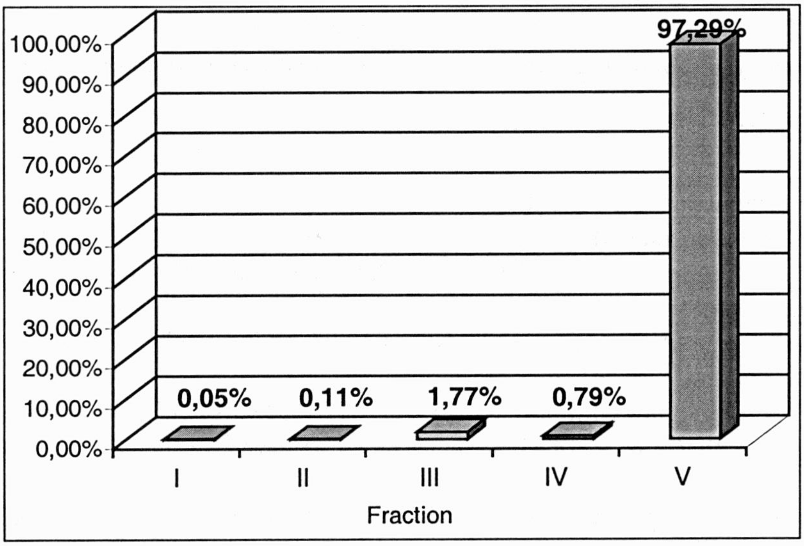

Fig. 2. Contributions of particular fractions to the total content of aluminium, mean values from all the samples studied

A total content of aluminium in the samples tested varied in the range from 11 g/kg to 41 g/kg (mean of 19.5 g/kg) (figure 2). The contributions of fractions I and II, the most mobile and the most easily bioavailable ones, in a total content of aluminium were small and did not exceed 0.1% (mean of 0.046%) for fraction I and 0.6% (mean of 0.105%) for fraction II. A comparison with analogous earlier results obtained for the bottom sediments from the Lake Jarosławieckie, lying in the area of the Wielkopolski National Park, shows that in the lake bottom sediments the contribution of these two fractions was greater [1]. The most probable reason was that the lake bottom sediment made of much finer grains was characterised by much higher ratio of the surface area of particular grains to their mass. It is known that extraction conducted in very mild conditions releases only the aluminium from the surface of the grains; for fraction I it follows directly from its definition. Hence, lower content of fractions I and II in the river bottom sediments of coarser grains is fully justified. The content of aluminium in fractions III and IV was greater. The contribution of fraction III to a total content of aluminium in the samples studied did not exceed 8.8% (mean of 1.77%), while that of fraction IV – 2.20% (mean of 0.79%). From among the four bioavailable fractions, the contribution of fraction III, bound with hydrated iron and manganese oxides, was the greatest. This observation is fully justified as in the alluvial sediments the content of metals in this fraction is usually the greatest. It is reasonable to expect that in the dynamic system of a river, the first two fractions will be easily released to bulk water, in contrast to the lake. The aluminium in fraction III is less mobile, so its release into the bulk water is more difficult. It could occur in strongly reducing conditions near the bottom zone, which is rather unlikely in a flowing river whose water is oxidised and strongly mixed. A lower contribution of aluminium to fraction IV bound to organic matter is a consequence of its low content in alluvial sediments in general. In the samples of a higher content of organic matter, the contribution of fraction IV to a total content of aluminium increased. In the bottom sediments from the Lake Jarosławieckie, the contribution of aluminium to fraction IV was the greatest [1]. However, in the bottom sediments from this lake the contribution of organic matter to a total mass of the sediment was much greater. The organic matter is characterised by highly developed surface on which metals can sorb, which has been observed in the study of the species of other metals [5]. In the bottom sediments from the Odra river, the contribution of aluminium from fraction V was by far the greatest, practically unavailable for living organisms. On average 97.29% of the total aluminium content in the Odra river sediments occurred in fraction V.

4. SUMMARY

Aluminium is a typical macrocomponent of bottom sediments. Release of even a small per cent of its content into bulk water can lead to a significant increase in its concentration. In adverse conditions, it can be a threat to the whole ecosystem. Such conditions can occur, e.g., in a strongly polluted river at a decreased pH (release of fractions I and II) or in anaerobic reducing conditions (release of fraction III). In view of the results of our study, such a threat does not exist in clean and well aerated rivers.

REFERENCES

[1] SOBCZYŃSKI T., PEŁECHATA A., ZIOŁA A., PEŁECHATY M., BURCHARDT L., SIEPAK J., *Accumulation of aluminium in the freshwater ecosystem of Jarosławieckie Lake*, Polish Journal of Environmental Studies, 2002, Vol. 11, Suplement, 177–82.

[2] TESSIER A., CAMPBELL P.G., BISSON M., *Sequential Extraction Procedure for the Speciation of Particulate Trace Metals*, Anal. Chem., 1979, 51 (7), 844–851.

[3] OSTROWSKA A., GAWLIŃSKI S., SZCZUBIAŁKA Z., *Metody analizy i oceny właściowości gleb i roślin*, Instytut Ochrony Środowiska, Warszawa, 1991, 87–93.

[4] ELBANOWSKA H., ZERBE J., SIEPAK J., *Fizyczno-chemiczne badania wód*, Wydawnictwo Naukowe UAM, Poznań, 1999, 145–148.

[5] SOBCZYŃSKI T., SIEPAK J., *Speciation of Heavy Metals in Bottom Sediments of Lakes in the Area of Wielkopolski National Park*, Polish Journal of Environmental Studies, 2001, Vol. 10, No. 6, 463–474.

FRAKCJONOWANIE GLINU W OSADACH ALUWIALNYCH

Przedstawiono wyniki badań nad zawartością glinu w osadach dennych środkowej Odry. Oznaczano zarówno całkowitą zawartość tego metalu, jak i pięciu jego form, różniących się mobilnością, a tym samym i dostępnością dla roślin. Frakcjonowanie realizowano za pomocą ekstrakcji sekwencyjnej według schematu zaproponowanego przez Tessiera. W ekstraktach glin oznaczano metodą atomowej spektrofotometrii absorpcyjnej. W badanych osadach całkowita zawartość glinu wynosiła średnio 1,95 g/kg. Metal ten był trwale unieruchomiony w osadzie, a tylko średnio 1,77% ogólnej jego zawartości było związane z frakcją uwalnianą do toni w warunkach silnie redukujących.