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Immobilization of Scandium and Other Chemical Elements in Systems with Aquatic Macrophyte

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Abstract—The possibility of immobilization of scandium and other chemical elements by biogenic materials derived from an aquatic macrophyte was explored. The concentrations of scandium and some other chemical elements were measured in the dried biomass (mortmass) of aquatic plants *Myriophyllum aquaticum*. In the experiments, the mortmass was incubated in aquatic systems where some chemical elements were added to the aquatic medium. After the incubation, the concentrations of these chemical elements in the mortmass were measured using inductively coupled plasma atomic emission spectroscopy (ICP-AES), also referred to as inductively coupled plasma optical emission spectrometry (ICP-OES). Increases in the concentrations of scandium and some other chemical elements (Ce, In, Se, Ru, Pd, U, and Zr) were observed in the biogenic material.

Keywords: scandium, cerium, palladium, zirconium, titanium, europium, ruthenium, selenium, indium, uranium, macrophytes, aquatic plants, parrot feather, *Myriophyllum aquaticum*, inductively coupled plasma-optical emission spectrometry

INTRODUCTION

The monograph “The Biosphere” and other publications by V.I. Vernadskii devoted considerable attention to biogenic migration of chemical elements, which issues remain topical today. Biogenic migration of elements [1–3] is essential for the formation of the geochemical environment and elemental composition of the components of ecosystems. The roles of the different components of ecosystems in migration of elements were elucidated, and the biotic and abiotic components of the environment were analyzed for elemental composition [3]. A large body of information has been accumulated concerning the toxicity of some chemical elements [3]. Studies of the quantitative characteristics of the processes and phenomena associated with migration of elements are still relevant today because of the environmental pollution issues prioritized in the context of human impacts on the biosphere under current conditions [2, 3, 5–12]. Previously, the ability of the biomass of aquatic macrophytes to immobilize certain elements was demonstrated using the example of *Ceratophyllum*

demersum L. macrophytes and gold (Au) nanoparticles [13]. Also, the ability of biodebris to immobilize rare-earth elements was revealed [14].

Here, we report the results of experiments that aimed to continue the efforts in the direction outlined above and test the hypothesis of the ability of mortmass of parrot feather watermilfoil [*Myriophyllum aquaticum* (Vell.) Verdc.], an aquatic macrophyte widespread in several continents, to immobilize chemical elements occurring in an aquatic medium: scandium, titanium, zirconium, palladium, and some others. These experiments gave positive results that confirmed the validity of the hypothesis tested. This publication is based on several scientific papers presented by us at the meeting of the Bureau of the Department of Earth Sciences, Russian Academy of Sciences (2014) and Biogeochemical Readings to Memorize V.V. Koval’skii (Vernadskii Institute of Geochemistry and Analytical Chemistry, Russian Academy of Sciences, 2012–2014), as well as in Moscow State University and the University of Massachusetts in Amherst (the United States).

EXPERIMENTAL

Samples of mortmass of parrot feather watermilfoil *Myriophyllum aquaticum* (Vell.) Verdc. (Haloragaceae family) were incubated in aqueous systems with the volume of 1 L. The water used in our experiments was purified in Barnstead Nanopure Ultrapure Water System and had a characteristic 18 MΩ/cm.

Adding the elements of interest to the aqueous medium resulted in the following concentrations, mg/L: 0.5 for scandium, ruthenium, and palladium; 1 for indium, zirconium, and uranium; and 2 for cerium, europium, and selenium. Titanium oxide (TiO₂) nanoparticles were added into the aqueous medium to the concentration of 20 mg/L.

The following chemicals were used for the measurements: standard scandium solution: Plasma Emission Standard, Spectrum®; 1000.2 ppm (1000.2 µg/mL) in 5% nitric acid, Spectrum Chemical Mfg Corp., Gardena, CA 90248, USA; standard titanium solution: Perkin Elmer Pure Atomic Spectroscopy Standard; Lot no. 8-130TI-PE (Perkin Elmer Instruments); standard palladium solution: Plasma Emission Standard, Spectrum®; 999.2 ppm (999.2 µg/mL) in 20% HCl; Spectrum Chemical Mfg Corp., Gardena, CA 90248, USA; standard zirconium solution: 1000 ppm (1000 µg/mL) in 10% HCl; Spex Industries, Inc., Edison, NJ 08820, USA.

Standard solutions of other chemical elements were used in a similar way.

The TiO₂ nanoparticles used in the experiments had the following characteristics: diameter 50 nm, specific surface area 325 m²/g (Zhejiang Hongsheng Material Technology Co., China).

The duration of the incubation at 20°C was 24 h.

The concentrations of the chemical elements were measured by inductively coupled plasma optical emission spectrometry (ICP-OES) on a Perkin-Elmer Optima 3000 DV spectrometer.

RESULTS AND DISCUSSION

Our experiments produced the following results. As Table 1 shows, the concentrations of the chemical elements of interest in the mortmass of the aquatic plant species *Myriophyllum aquaticum* increased after the incubation.

According to Table 1, the palladium content in the control sample of *Myriophyllum aquaticum* mortmass (which was incubated in an analogous aqueous system without palladium added to the aqueous medium) was 1.89 ± 1.27 µg/kg. After the mortmass incubation in a palladium-containing aqueous medium the palladium content in the *Myriophyllum aquaticum* mortmass sample increased 5 times to reach 9.59 ± 1.09 µg/kg.

Likewise, the concentration of scandium increased as a result of the incubation. In the control sample the scandium content was 0.09 ± 0.002 µg/kg. After the incubation in a scandium-containing aqueous medium the concentration of scandium in the *Myriophyllum aquaticum* mortmass increased almost 200 times to 18.85 ± 2.19 µg/kg.

The titanium content in the mortmass control samples was 0.11 ± 0.03 mg/kg, on the average. After the incubation in the aqueous medium with titanium added, the titanium content in the *Myriophyllum aquaticum* mortmass increased more than 500 times and reached 59.11 ± 33.98 mg/kg.

The concentration of zirconium in the control mortmass was 0.19 ± 0.15 mg/kg. After the incubation in an aqueous medium with zirconium added the zirconium content in the *Myriophyllum aquaticum* mortmass increased by nearly 2 orders of magnitude and reached 15.48 ± 9.1 mg/kg.

Our experiments on the accumulation of a number of other chemical elements also revealed a significant increase in their concentration in the mortmass after incubation. In the control samples of the *Myriophyllum aquaticum* mortmass the concentrations of cerium (Ce), europium (Eu), indium (In), ruthenium (Ru), selenium (Se), and uranium (U) were below the corresponding detection limits. After the incubation in the aqueous medium into which these chemical elements were added their concentrations in the *Myriophyllum aquaticum* mortmass exceeded the detection limits (see Table 1).

The concentrations of a number of chemical elements in plant samples, determined in our experiments, agree with published data on the measured concentrations of these chemical elements in plants (see Table 2).

Among the chemicals elements analyzed in this study was titanium which was introduced into the aqueous phase in the form of TiO₂ nanoparticles.

The new facts about the immobilization of titanium by the mortmass of *Myriophyllum aquaticum* macro-

Table 1. Immobilization of chemical elements by mortmass of aquatic macrophyte *Myriophyllum aquaticum*

Chemical elements	Upon addition of the chemical elements in the aqueous phase and subsequent incubation, average	St. Dev. ^a	Control, average	St. Dev. ^a
Cerium, µg/kg	60.00	24.37	Below detection limit	–
Europium, µg/kg	51.46	18.95	Below detection limit	–
Indium, µg/kg	19.59	5.97	Below detection limit	–
Palladium, µg/kg	9.59	1.09	1.89	1.27
Ruthenium µg/kg	5.60	2.05	Below detection limit	–
Scandium, µg/kg	18.85	2.19	0.09	0.002
Selenium, µg/kg	12.56	7.94	Below detection limit	–
Titanium, mg/kg	59.11	33.98	0.11	0.03
Uranium, µg/kg	22.67	6.02	Below detection limit	–
Zirconium, mg/kg	15.48	9.01	0.19	0.15

^aSt. Dev. is standard deviation.

Table 2. Measured concentrations of some of the chemical elements analyzed in this study in the biomass and in other samples of biogenic plant material (as reported by different researchers)

Chemical elements	Samples of material, plants species	Concentration (dry weight)	References
Scandium	Various species	The concentrations detected were at the level of several micrograms per kilogram (ppb)	[16]
Palladium	<i>Pinus radiata</i>	15 ± 15 ppb in ash. Ash accounted for 3% of the dry weight of the samples	[6]
Zirconium	<i>Lycopersicon esculentum</i> L.; <i>Pisum sativum</i> L.	1–8 mg/kg	[17]
Palladium, scandium, zirconium, titanium	<i>Myriophyllum aquaticum</i>	Content of chemical elements in the mortmass of <i>Myriophyllum aquaticum</i> (see text)	This study

phyte, that we reported herein, are consistent with the previously published data on binding several kinds of nanoparticles by organic matter [12].

In analyzing the results it is useful to remember that the immobilization of chemical elements by the mortmass of *Myriophyllum aquaticum* occurring in an aqueous medium entails the corresponding decreases in the concentrations of these elements in the aqueous phase. Thereby, a contribution is made to the removal of the chemical elements from the aqueous medium. Thus, the phenomenon under study fits into the water self-purification processes characterized in [4, 7–12]. We emphasize the importance of water self-purifica-

tion to remove nanoparticles, because toxicity of some kinds of nanoparticles was proven, e.g., in [15]. The role of the chemical elements of interest in the environment is a topical issue in view of their application in industry and in the manufacture of various products and materials, whereby new types of pollution of the biosphere and hydrosphere, including freshwater bodies (water bodies and watercourses), inevitably emerge.

The data on immobilization of chemical elements by biogenic material, obtained by us, may be useful in the future for the development of innovative biotechnologies and environmentally sound technologies for

treatment of contaminated aqueous media, wastewaters, and aquatic ecosystems (water bodies and watercourses).

CONCLUSIONS

(1) The results obtained contribute to the accumulation of facts about the biogenic migration of chemical elements (these scientific topics received much attention from Vernadskii in whose publications the term “biogenic migration of atoms” was of often use).

(2) Based on new examples [mortmass of widespread parrot feather watermilfoil (*Myriophyllum aquaticum*) as biogenic material], our studies confirm that the mortmass of aquatic plants, which is a component of natural ecosystems, along with other components [13, 14] can fulfill the function of a depot or a site for immobilization, deposition, and sequestration of chemical elements (e.g., scandium, zirconium, titanium, cerium, europium, indium, ruthenium, selenium, palladium and uranium).

(3) The new facts presented here are consistent with the theory of the multifunctional role of the biota in the self-purification of water (see [4, 7–11]) and with the concepts of the Ostroumov’s typology of the functions of the matter in the biosphere and the environment (geochemical environment).

(4) Through revealing the immobilization of titanium upon addition of TiO₂-containing nanoparticles to the aqueous medium, our experiments contribute to the accumulation of facts about nanomaterials, specifically, about biogenic migration of chemical elements added in the form of nanoparticles, migration of metal-containing nanoparticles (by the example of titanium oxide nanoparticles) when entering the environment (including aquatic medium).

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