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Elemental Composition and Intensity of the Accumulation of Chemical Elements in the Leaves of Siberian Sea Buckthorn (*Hippiophae rhamnoides* L.)

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Abstract

The elemental structure of green leaves of Siberian sea buckthorn (*Hippophae rhamnoides* L. ssp. mongolica Rousi) growing under endemic conditions of the West Siberia was studied. The simultaneous quantitative content of K, Ca, Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Se, Br, Rd, Sr, Y, Zr, Nb, Mo, Pb in green leaves and soil, as well as coefficients of biological absorption of these elements were determined by the method of RFA-SR (X-ray fluorescence analysis using synchrotron radiation). Species-specific absorption features of elements by leaves of sea buckthorn were revealed, what was expressed in the increased accumulation of vitally necessary chrome and elements with unidentified biological role: niobium, scandium, titan, zirconium and strontium, relatively to the terrestrial phytomass. It was shown that leaves of Siberian sea buckthorn could serve a food source of vitally necessary chromium and manganese in the form of the easily digestible biogenic form. It was established that fruits of sea buckthorn do not concentrate toxic chemical elements: lead and arsenic..

Key words: elemental structure, synchrotron radiation, leaves of sea buckthorn

INTRODUCTION

Recently, leaves of sea buckthorn (*Hippophae rhamnoides* L.) attracted increased attention of pharmacologists, since almost the same complex of biologically active organic substances (BAS), as in the fruits was discovered in them [1]. It is known that the activity of many vegetable BAS of the phenolic family is revealed itself only in the form of organomineral complexes [2–4]. Leaves of sea buckthorn contain a great amount of phenolic compounds and they are used in the production of a variety of therapeutic and preventive action, including radioprotective preparations [5, 8].

The mineral content of leaves of Siberian sea buckthorn (*Hippophae rhamnoides* L. ssp. mongolica) has not been fully studied nowadays. Thus, the residual concentration of essential elements (K, Ca, Fe, Mg, Zn, Cu and Co) in oil-seed meal from leaves of Siberian sea buckthorn after the extraction of fat-soluble substances was determined [7]. Concentrations of K, Ca and Mg in integral leaves of Siberian sea buckthorn grown in the middle zone of Russia are known [8].

At the same time, there is no information on the accumulation intensity of soil elements in sea buckthorn leaves. This information is very important, when one speaks of the use of leaves when formulating alimental and medical and preventive products [1], especially, in case of the plant cultivation on soils with a high content of toxic elements, viz, arsenic, lead *etc*. [9]. A highly sensitive method that provides their simultaneous quantitative determination is preferred for the adequate analysis of the content of the whole complex of elements in one sample of the material. The XRF method analysis using synchrotron radiation (XRF-SR) allows determining quantitatively the content of elements in the diapason of atomic masses from potassium to uranium, regardless their ratio in the material, without the necessity to reduce to ash the sample previously [10, 11].

The goal of this research is the qualitative determination of the elemental composition of leaves of Siberian sea buckthorn and identification of patterns of absorption of individual elements from soil by leaves.

MATERIALS AND METHODS

Average samples of leaves of sea buckthorn of four selection varieties of Institute of Cytology and Genetics (ICG) of the SB RAS (Novosibirsk) generated on the ground of the gene pool of the populations of Altai: "Zarnitsa", "Zyryanka", "Krasny Fakel", "Sibirskiy Rumyanets" [12] were collected in the growth phase of formed fruits from plants growing on the overall plot. Leaves were dehydrated in a drying oven up to the constant weight at 105 °C, grinded at the propeller type mill at 10 000 min^{-1} for 30 s and sieved through a capron sieve with the cells size of 0.5×0.5 mm to remove large particles.

Simultaneously with leaves, average soil samples were selected directly from under plants studied with the depth of the greatest density of the rhizosphere (10–15 cm lower the layer of the organic litter, soil horizon A1–A2). The soil type is grey forest, pH 5.5. It was dehydrated at 105 °C to the constant weight. To avoid the abrasive skid of elements from the metallic knife of the mill, soil samples were pulverized in a porcelain mortar and sieved through a capron sieve with the cell size of 0.5×0.5 mm.

The element composition of leaves and soil was determined by the XRF method analysis using the synchrotron radiation (SR RFA). Measurements were conducted at the station of elemental analysis at the Siberian Center of the Synchrotron and Terahertz Radiation of the Budker Institute of Nuclear Physics, SB RAS (Novosibirsk) on the VEPP-3 electron storage ring by the method described in work [10].

A tablet of the weight of 30 mg and diameter of 1.0 cm was formed from the powder mass of the sample prepared for the analysis in a special press-form was formed. The sample in form of a tablet was placed into fluoroplastic rings between two chemically pure films of the thickness of 5 μm, and then irradiated. Spectra of characteristic XRF were received at the irradiation of samples with the excitation energy of 23 keV. For the quantitative analysis XRF spectra were processed using the software package AXIL (QXAS, IAEA).

As external standards, as closest on the composition to the definable samples, Russian standards were used: of cereal grass mixture SORM1 GSO 8242–2003 for plant tissues and BIL-1 GSO 7126–94 for soil samples.

The quantitative content of 22 chemical elements was investigated: K, Ca, Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Se, Br, Rb, Sr, Y, Zr, Nb, Mo, and Pb.

The coefficient of biological absorption (CBA) of each element from soil by leaves was determined as the ratio of concentration [13]: $CBA_A = (C_{A/0}/C_{A/s}) \cdot 100$ %, where A is the chemical element, $C_{A/0}$ is the concentration of the element in a dry substance of leaves; $C_{A/s}$ is the concentration of the element in soil.

As the reference standard, for the comparison, literature data on the average terrestrial phytomass, representing a sum of aboveground and underground parts of plants of the earth surface were used as the standard [13–15]. The overall assessment of absorption of chemical elements by various tissues of sea buckthorn in the form of the index of biological absorption is presented by us in the work [16].

The degree of satisfaction of needs of the human organism in microelements was determined according to the official norms of physiological needs in energy and nutrients for various groups of the population of the Russian Federation [17].

RESULTS AND DISCUSSION

Clarkes of elements differ by million times, for this reason, elements were divided into three groups.

1) group A – the concentration of elements in the earth's lithosphere exceeds 100 μg/g;

2) group B – from 10 to 100 μg/g;

3) group C – less than 10 μg/g.

Data on the content of elements in soil and the dry substance of leafs of sea buckthorn are given in Table 1. The average concentration of elements in the phytomass of the Earth is also indicated for comparison [14].

Elements of group A

Iron. Concentrations of iron are maximal, relatively to the rest of microelements and reach 180 μg/g. This is conditioned by the participation of the vital element in the implementation of many functions of both animal and vegetable organisms, in the first place, in photosynthesis. Despite the small coefficient of its absorption from soil (CBA_{Fe} < 0.8 %), the required level of iron is provided in green leaves [2]. The content of iron in the leaf oilseed maalox sea buckthorn is comparable with its content in leafs and it contains 381–411 μg/g.

TABLE 1

Absolute concentration of elements, coefficient of the biological absorption by the phytomass and leaves (CBA_p and CBA_l, respectively) and proportion of the daily requirement (PR) of a man (content in 10 g of dry leaves)

Elements	Earth's soil, ppm *	ICG** soil, μg/g	CBA_p, %	Leaves		
				Content, μg/g	CBA_l, %	PR, %
			Group A			
Fe	40 000	23525±938	0.35	186±30	0.78±0.08	19
K	14 000	15462±907	100	7406±204	46.7±2.8	2.9
Ca	15 000	13033±946	120	21490±1897	168±13	21
Ti	5000	4623±276	0.02	6.67±1.53	0.145±0.022	n/d
Mn	1000	772±30	63	127±6.1	16.7±1.2	67
Zr	400	348±88	0.2	3.5±1.0	1.27±0.16	n/d
Sr	250	171±5	10	68.7±7.1	39.9±4.4	n/d
			Group B			
Zn	90	45.5±0.9	111	19.0±4.5	41.8±10.9	1.6
V	90	87.3±9.4	1.8	0.27±0.07	0.33±0.12	n/d
Cr	70	65.5±6.9	0.3	2.00±0.70	2.73±0.71	39
Ni	50	42.5±2.4	6.0	1.67±0.22	4.16±0.83	n/d
Rb	35	60.0±3.3	57	5.27±0.45	8.48±0.78	n/d
Cu	30	20.0±1.1	47	2.40±0.17	12.3±1.8	2.5
Y	30	23.3±1.2	–	0.64±0.26	2.86±1.34	n/d
Pb	12	11.3±0.1	23	0.81±0.13	7.07±1.21	n/d
Nb	10	11.0±1.3	0.2	0.41±0.10	3.79±1.21	n/d
			Group C			
Sc	7.0	4.75±1.65	0.11	0.027±0.003	1.2±0.54	n/d
Co	8.0	9.75±0.25	6.3	0.073±0.012	0.76±0.14	7.1
As	6.0	6.28±0.46	3.3	0.11±0.03	1.67±0.26	n/d
Se	0.4	1.53±0.62	50	0.18±0.05	9.87±1.86	2.5
Br	10	4.38±0.61	150	5.53±2.22	149±57	n/d
Mo	1.2	0.56±0.13	75	0.067±0.009	15.7±1.4	1.0

Notes. 1. n/d – not determined. 2. Line – no literature data.

*By Bowen, 1966 (cit. by [15]).

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Calcium is actively accumulated by leaves of Siberian sea buckthorn. The intensity of accumulation in leaves exceeds the phytomass by 1.4 times and soil concentration by 1.7 times, on the basis of what sea buckthorn can be referred to plants, which are concentrators of calcium in leaves. Herewith, the element content is identical under endemic conditions and conditions of the introduction in the midland of Russia [8].

Potassium, one of the most mobile elements of the soil solution, penetrates well into leaves of sea buckthorn. Its concentration here reaches 7400 μg/g. The introduction conditions almost do not impact this indicator [8].

Titanium. Despite a relatively high content of titanium in soils (4600 μg/g), it is absorbed very poorly by plants [13]. Nevertheless, leaves of sea buckthorn accumulate this element with the intensity that exceeds by seven times the accumulation by the ground phytomass. A similar phenomenon is observed by us when studying of the elemental composition of fruits [18].

Manganese. The total content of this vital element in leaves of sea buckthorn reaches 130 μg/g, while only less than 50 μg/g of manganese was found in degreased oilseed meal [7], even less in fruits, 17 μg/g [18].

Zirconium is characterized by a relatively small (3.5 μg/g) concentrations in leaves. Herewith, its coefficient of absorption by leaves exceeds the indicator for the phytomass by 6 times and by 4 times for fruits [18].

Strontium is a chemically close analog of calcium [13]. However, its absorption by leaves of sea buckthorn is greater by 4 times, in comparison with the absorption by phytomass and by 20 times, in comparison with the absorption by fruits of buckthorn [18].

Elements of group B

Zink. It is characterized by a relatively high intensity of the accumulation among other chemical elements of the group. About 20 μg/g of this essential element was found in leaves of Siberian sea buckthorn, the same amount is also contained in fruits (18.8 μg/h) [18], while from 43 to 95 μg/g was detected in the leaf oilseed meal [7].

Chromium. It refers to essential elements with a low coefficient of absorption (about 0.3 %) [15]. However, leaves of sea buckthorn accumulate it almost 10 times more intensively, in comparison with the phytomass. This fact is interesting in terms of the possible use of leaves of sea buckthorn as a natural source of biogenic chromium.

A similar character of the absorption by leaves was found and for the element with not yet established biological role – **niobium.**

Nickel. Its absorption and concentration in leaves of sea buckthorn are not high and somewhat lower the average indicator of the phytomass.

Cuprum. The absorption of this vital element by leaves of sea buckthorn is considerably lower, in comparison with phytomass. The data received by us on its content in leaves of sea buckthorn (2.40 μg/g) are close to those for the leaf oilseed meal (2.6–4.0 μg/g) [7].

Lead and rubidium. The terrestrial phytomass accumulates lead and rubidium with a moderate intensity: CBA is equal to 25 and 57 %, respectively. However, they are accumulated in leaves of Siberian sea buckthorn only of 7–8 % from the soil content.

Elements of group C

Bromine. The content of bromine in leaves of sea buckthorn exceeds the soil content. The phenomenon of excessive accumulation of this element by land plants is known for a long time; however, it has not received yet the biological explanation [15]. Sea buckthorn is not an exception: the intensity of accumulation of this element in leaves is 150 %.

Cobalt. The concentration of the element in leaves is extremely low – 0.073 μg/g. In leaf oilseed meal [7] and fruits of sea buckthorn [18], cobalt is present in trace amounts, while the average phytomass accumulate it at the level of 0.5 μg/g [14]. This indicates the presence of an active biological barrier for this element's penetration in leaf tissues of sea buckthorn.

Molybdenum is present in the concentration of 0.07 μg/g, what is considerably lower, in comparison with its content in fruits (0.25 μg/g) [18].

Selenium and arsenic. The concentration of these elements in leaves of sea buckthorn (0.18 and 0.11 μg/g, respectively) is virtually identical to their concentration in fruits: 0.20 and 0.13 μg/g, respectively [18].

CONCLUSION

The elemental composition of 22 chemical elements: K, Ca, Sc, Ti, V, Cr, Mn, Fe, Co. Ni, Cu, Zn, As, Se, Br, Rb, Sr, Y, Zr, Nb, Mo, Pb was determined for the first time by the method of RFA-SR and the quantitative content in leaves of Siberian sea buckthorn (*Hippophae rhamnoides* L.) was identified and the absorption intensity of these elements from soil was also discovered.

It was established that leaves of Siberian sea buckthorn were characterized by the selective accumulation of individual chemical elements, relatively to their soil composition. The accumulation of calcium and bromine is excessive; absorption of other elements from soil is relatively weak and comparable to the indicator for the average terrestrial phytomass. Along with that, species-specific features in the accumulation of individual elements by leaves were found. Thus, relatively to the earth's phytomass, the accumulation of vital chromium and elements with the unidentified biological role: niobium, scandium, titan, zirconium and strontium is increased by many times.

Leaves of Siberian sea buckthorn can serve as the real source of vital elements, as an easily digestible biogenic form [4]: in 10 g of a dry substance, there contained approximately 70 % of the daily need of a person in Mn, up to 20 % of Ca and Fe, up to 40 % of Cr. Herewith, it is important to note that leaves of sea buckthorn do not accumulate such toxic elements, as arsenic and lead.

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