The role of selenium deficiency in the biogeochemical food chains

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Abstract: *Comparative researches of the Se migrational ways in different regions of the biosphere, with describing singularities of the biosphere zone biogeochemical cycles of Se. Special attention is given to coefficients of biological absorption of Se in a system: environment-organism. Obtained massive data is related to a development of endemic Se pathologies. The involving of Se in biogeochemical cycle depends on geological soil-type, secondary processes such as weathering and leaching Se mobile forms etc.*

Key words: *Se-deficiency, biogeochemical provinces, biogeochemical food chains, biogeochemical cycle*

INTRODUCTION

Selenium is a bioessential halcophilic element. Its average content in the soil amounts to 50 ppb [15]. This element is often concentrated in some geochemical places and sediments. Black organogenic limestone, for example, contains about 675 ppm Se.

In the non-chernozem zone, extending from northeast boundaries of USA, through Europe - north Germany, Denmark, Poland, through Baltic countries, Central Russia - on Ural, further through all Siberia up to east boundaries of Russia (the sites of distribution of podzolic, soddy podzolic, and some boggy soils) most frequently meet the biogeochemical provinces with deficiency of Se-bioessential trace element with unique biological functions and wide spectrum of biological effect [8, 10, 11, 15, 17, 18, 19, 23].

The essential trace mineral selenium is of great importance to human health. Taken up from the soil, Se enters to the food chain. Animal protein is the main source of dietary Se, accounting for 66% of the total Se intake in Europe. In many parts of the world the concentration of selenium in the soil is < 0.5 ppm, so the risk of Se-deficiency and the associated detrimental health effects are considerable.

Se-dependent enzymes, such as glutathione peroxidase, maintain nitric oxide in its reduced form and protect against oxidative stress. Via this mechanism, Se-deficiency might predispose to cardiovascular disease [21].

Selenium plays a major role in the biosphere taking into account the presence of the whole class of 30 selenium containing and Se dependant enzymes and wide spreading of Se-deficiency diseases (tabl.1). Se deficiency causes many diseases, and very dangerous Keshan disease, which occurs in north-eastern China. It is closely related to the Se content in drinking water and grain-crops. The Se content in the grain-crops obtained from the unfavorable zone was found to be Se free. The white muscle disease is the Se-deficiency that caused pathology in animals.

Table 1: Causes of Se deficiency and symptoms of diseases

Causes of Se deficit	Targets	Symptoms	Indicators of deficit
Inadequate nutrition (deficit of protein and fat)	Immune system	Flu and inflammation; increased risk of the occurrence of tumor	Blood plasma
Liver disease (hepatitis)	Cardiovascular system	The risk of myocardial infarction; myocardial dystrophy	Hair
Influence of As and toxic metals (Hg, Pb, Cd)	Liver	Reduction of desintoxication function and protein synthesis; hiperholesteronemy	Nails
Radiation	Thyroid gland	Reduced function (T3, T4)	Activity of glutathione-reductase
Disbacteriose hoses	Skin	Dermatitis, eczema, inflammatory processes	Blood
Low content in the soil, water and food	Hair	Damaged hair, weak growth hair	Hair
Alcoholism	Liver	Dystrophy	Nails

Biogeochemical and metabolic interactions as occurred between I and Se are of special interest. It is practically impossible to prevent thyroid adenoma and cretinism through taking I additives to a diet in the case of Se deficiency background. In this case the Se deficiency causes decrease in I thironine-deiodinase, so that the correction by I intake appears ineffective. Organism reactions to Se deficiency in the environment and food chains are shown in Fig. 1.

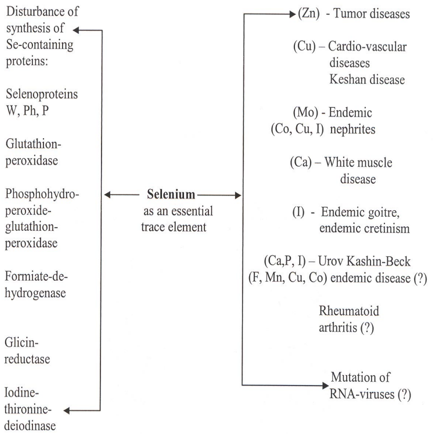

Fig. 1. Organism responses to Se deficiency in the environment and food chains. The chemical elements connected with Se metabolism are specified in brackets

The basic biochemical reactions catalyzed Se-enzymes:

GSH-Px: $$H_2O_2 + 2GSH \rightarrow 2H_2O + GSSG \quad (1)$$

GSH-Px: $$2ROOH + 2GSH \rightarrow ROH + GSSG + H_2O \quad (2)$$

GSSG-R: $$GSSG + NADPH + H \rightarrow 2GSH + NADP \quad (3)$$

The relationship of a trace element deficiency with the etiology of viral infections is of utmost importance. Non-virulent Coxsackie RNA virus B3 (CVB3/0) transformation into a virulent one was prevented in mice kept as Se deficient, this resulted from an irreversible mutation due to the genome structure variation. An endemic Keshan disease form of myopathy that is prevalent in some East Transbaikalia areas and China has a direct relationship to observed Se deficiency. Se-containing proteins and peptides are common in animals and humans where they control peroxide compounds, protein levels, nucleic acid, protein synthesis, lipid exchange, as well as spermatogenesis, vision processes and attention. Se-containing proteins prevent the development of endemic chondrodystrophy, prostatitis, pancreatitis, and possess a carcinostatic effect and radioprotective characteristics.

On the other hand, Se can become harmful to animals at high concentrations. The high Se biogeochemical provinces are rare but present in the Great Plain, of the USA.

This paper focuses on the regional distribution of Se and some questions of agricultural systems ecology, based on current experimental data and biogeochemical investigations.

SAMPLING AREAS AND METHODOLOGY

To investigate peculiarities of Se migration in arid, subarid and humid conditions, we have carried out biogeochemical studies of geochemically contrasting zones of Central Asia, Europe and Siberian regions. Later the route was from Moscow, to Tver - Novgorod; than - the Leningrad district, Karelia, Murmansk district, to Archangelsk etc. Besides the local territories in Moscow district, Chita and Voronezh district, South Ural, Northern Ossetia and in other Russian regions were taken.

METHODS AND RESULTS

The comprehensive ecology-biogeochemical methodology was used for regional and local investigation of selenium cycle involving complex of special methods of soil sciences, geobotany, soil microbiology, hydrogeochemistry, biochemistry and analytical chemistry. The sampling was performed by the method of conjugate sites. Soil forming rocks, different horizons of soil samples, alluvium deposits, surface river and lake waters, plants, amphibian, fishes, organs, and tissues of agricultural animals were collected and analyzed. Water samples were filtrated through filter paper and analyzed (precipitation - solid phase and liquid phase). Se content in different natural products was determined by a spectrofluorimetric method with 2,3-diaminonaphthaline using our modification of the known method by means of the standard samples analysis (soil, rocks) and the addition method of different Se compounds. The mean coefficient of variation (± standard error) of repeated analysis of the standard plant sample was 6.56 ± 0.62 per cent.

In water solutions selenium was determined by Flame and AA Spectroscopy methods.

To identify different Se forms in water, soil and plant extracts the methods of ion exchange and gel chromatography were applied. We used also the method of consecutive chemical fractionation developed by Chao and Sanzolone [7].

The different Se forms were determined in the extracts. According to the opinion of authors [7] the first form is the absorbed selenate and water-solution selenite migrating in soil and ground waters. The second part of whole Se is exchange selective absorbed selenite that it's available to plants. The third part is Se combined with metal's oxide, carbonate, and hydrolyzed organic substances as potentially available (assimilated) form of selenium for living organisms. The fourth and fifth parts of Se are that of sulphide and siliceous as inaccessible for organisms.

The data that we were obtained show significant discrepancies of Se in biogeochemical food chains and accumulation by organisms. The Chita district is a region with extremely low Se levels in all part of the chain. Se deficiency is due to very small Se content in soil-forming rocks (crystalline weathering granites, metamorphic sandstone). In this area there are frequent events of white muscle disease as well as Keshan disease and endemic Urov Kashin-Beck disease [10].

In north part of European Russia there is also a deficiency of this trace element, in spite of a normal Se content in rocks and soils. In both cases, the shortage of the element was attributable to the poor Se assimilation by plants from podzolic, bog, and peaty soils. The coefficient of biological absorption of Se by plants determined as a ration of microelement concentrations in plant and soil (Kb) is very low, less than 0.2 [8, 9].

Note should be taken on the Fergana valley as an arid subregion with optimal levels of Se in the environment. Here, Se is well absorbed by plants, Kb=1.5 and accumulated by organisms.

It was discovered the significance difference of Se distribution and accumulation in the environment of arid and humid regions. As appears from data (Table 2), the Se content in soilforming rocks of both regions is the same.

Table 2: Se content in basic parts of biogeochemical food chains of the arid and humid region of the biosphere [12]

Object of examination	**Selenium levels, ppb**	
	Arid region	Humid region
Soil-forming rocks (41)	100 - 35200	150 - 16000
Soils (215)	30 - 2070	300 - 2190
Plants (698)	10 - 1200	5 - 100
River waters (43)	0.20 - 4.0	0.04 - 1.6
Lake waters (19)	1.6 - 3.6	0.06 - 1.7

In brackets: number of samples.

However, Se levels in waters and plants of arid region are higher than that of humid region. For example, the Se content in plants of humid region is changed from 5 to 100 ppb on dry matter and the Se levels in grasses of arid region are varied from 10 to 1200 ppb. However both in arid region and humid that the low Se contents in rocks take place. As rule it is a zone of acidic intrusive rocks (for example, Issyk-Kul lake, Baikal lake, Chita district, some areas of Buryatia etc).

Alongside with the general peculiarities of a cycle of selenium in the biosphere, there are specific tendencies of rock formations with low concentration of Se and S. So, it is established, that the contents of S and Se in Cenozoic sedimentary rocks of Tunkin and Barguzin depressions are determined by the contents of organic substance and S, and in Chara and Baikal - organic substances (Fig. 2).

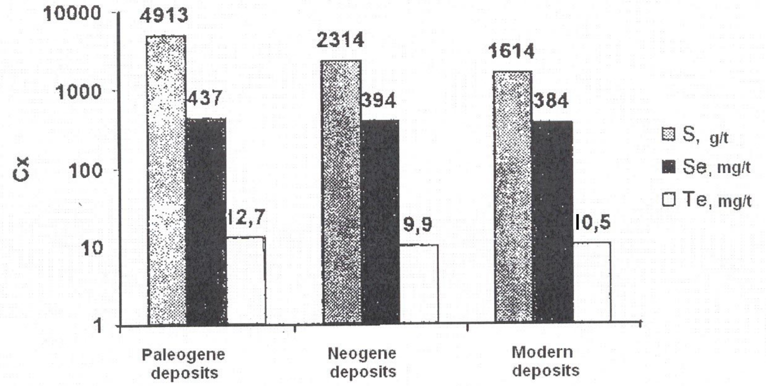

Fig. 2. Distribution of S, Se and Te contents in process of evolution of Cenozoic deposits [8].

The territory of Se deficiency reaches from Irkutsk up to Chara zone Chita district, covering Darkhat, Kosogol, Tunkin, South-Baikal, North-Baikal, Ust-Bargusin, Bargusin, Verkhangarsk, Tscipin, Muysk, Charsk, and Tokkinsk riftogenic depressions of rift zones [6]. The interval of Selenium concentration in soils of Listvyanka (the coast of Baikal), including alluvial, meadow, soddypodzolic and meadow boggy soils, is 44-297 μg/kg. It is appreciable below the average level of Se for soils of the world (300 μg/kg) [11].

In territory of the Western-Siberian lowland Se deficit is practically not shown, and concentration of Se in soils inherits the properties of parent rocks and decrease in a direction from the Kemerovo area (an ore zone) to Novosibirsk area [17]. In soils of Tuva and Altai concentrations of Se come closer to "clark" 300 μg/kg [16]. Nevertheless, under the contents of Se landscapes of each administrative unit are differentiated. In particular, it is typical of territories of Southern Ural, Tuva, Kamchatka and other areas of Russia.

In connection with the above data it should be taken in account migration of Se in systems: "organic" soils - plants. It is noted that in the most cases the assimilation of selenium by plants from "organic" soil is very low close to village Koldjat (Kazakhstan). So, the Se concentrations in the lower proterozoic carboniferous rocks of Trans Onega formations in Karelia (shungites) mounts to 11.6 ppm and Se content in plants are lower then 0.4 ppm. But in arid conditions at the zone of solanization gray soils with Se content of 2.2 ppm the concentration of Se in grasses is increasing sharply mounting to 70.0 ppm. The data show significance dependence of concentration of Se in plants from Se-mobile forms in soils determined by means of the method of consecutive chemical fractionation.

The defined tendency of higher accumulation of Se in ferriferous soil horizons is discovered: $r = +0,533 > r_{crit.}(1\ \%) = 0,302$ for $n=71$. The noticeable part soil Se was extracted by means of 4 M HCI simultaneous with Fe, Mn and other elements. The major part (about 90%) of soil Se was extracted with 0.1 M NaOH solution that is in line with observation of the Japanese scientists [18]. Hydroxide of Fe and Al adsorb the various Se compounds more effective. Thus, mobility of Se in soils in many respects depends on interaction of Se compounds with hydroxide of metals, humic acids and their salts (for example, with humate of iron) [10].

The biogeochemical regions are distinguishing not only the Se levels in the part of biogeochemical food chains but also by the capability to accumulate this microelement by different organisms (Table 3).

Table 3: Se accumulation by organisms in different natural conditions [12]

Organism	**Coefficient of biological accumulation (Kb)**	
	Arid region	Humid region
Insects	0.6 - 1.8	0.3 - 0.7
Amphibians	3.6 - 5.4	0.8 - 1.3
Fishes	5.9 - 6.3	1.4 - 1.9
Soil microflora	0.4 - 5.3	0.4 - 2.8
Plants	0.5 – 4.4	0.1 - 0.7

The intervals of Kb for humid region are more narrow and lower than ones of arid region. Thus the coefficient of biological accumulation of Se by animals, fishes, amphibian, mushrooms, plants and soil microorganisms from arid and humid regions were markedly differed. The intensity of biogenic migration of Se in various conditions does not depend on the content of the element in soils, it is bound up with adaptive properties of the investigated plants, which was shown on the example of 90 families and more 500 plant species. Among of pasture and meadow plants we didn't find selective Se accumulators. However mushrooms, especially tubular ones, puff-ball, garlic and agaric content have very high concentrations of this trace element. For example, in some kind of puff-ball enriched by proteins Se content is changed from 2 to 10 ppm [13, 14]. The metabolic ways of Se in the biosphere is given on Fig. 3.

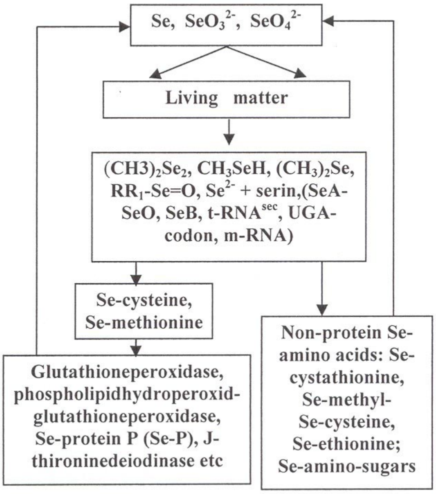

Fig. 3. The basic metabolic ways of selenium in the biosphere

As a whole, natural waters (rivers, lakes) don’t contain enough Se. In most cases Se concentration in river waters, as well as in an atmospheric precipitation, does not exceed 0.2 µg/l. Waters with higher mineralization contain higher concentration of Se (Fig. 4).

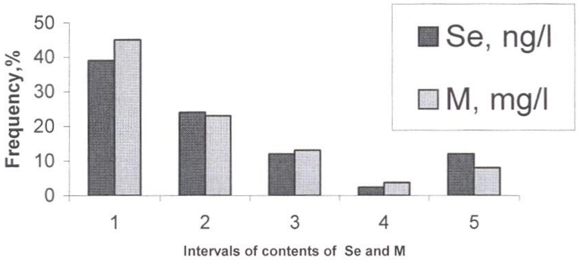

Fig. 4. Frequency of occurrence of concentration of selenium (Se, ng/l) and level of a mineralization (M, mg/l) in natural waters of East Transbaikalia. 1) ≤ 100; 2) > 100-150; 3) > 150-200; 4) > 200-300; 5) >300.

CONCLUSION

The biological roles ascribed to Se include the prevention of cancer [5], cardiovascular disease [4, 22] and viral mutation [2]. In addition the trace element is essential for optimal endocrine and immune function and moderating the inflammatory response [1, 3, 20].

By consideration of behavior of Se in the biosphere, it is necessary to emphasize importance of an evolutionary estimation of migration of Se at formation of the biosphere, belonging of this element to the certain geological formations, an essential role of an atmospheric component in a biogeochemical cycle of the Se, expressed geochemical connection Se and sulphur, Se and iron, Se and organic substance. In ecological aspect the genetic factors causing character of its metabolism are extremely important knowledge of interaction of Se with others macro- and microelements in various organisms. Results of researches are a part of basis for formation of a global cycle of Se. They are necessary for practical recommendations of preventive maintenance of selenium deficiency and for updating biogeochemical criteria of an ecological estimation of territories.

1. The obtained results show an essential role of Se in both animal and human health status. A certain significance of man-caused factors in the manifestations of selenium deficiency-based pathologies has been determined.

2. Se-deficient territories are most frequently observed in an extensive region of non-chernozem zone. This phenomenon is attributed both to the selenium low content in rocks and its weak assimilation by plants growing on podzolic or peat soils.

3. Some man-caused factors, like application of the phosphoric and nitric fertilizers, increased metal migrations resulted from intensive land use are also play an essential role.

4. The principal causes of Se-deficiency depends on the contemporary conditions of the agroecosystems development are as follows:

– Extensive type of agricultural activities connected with intensive land use and changes as occurred in selenium biogeochemical cycles.

– Drastic increase of man-caused component in natural-technogenic cycles of metals and radionuclides is of significant importance.

– Se-deficiency is also connected with the evolution in nutrition and the increase of a role of antioxidants. Se compounds have the principal significance among them.

– Se-deficiency genesis is primarily connected with the parameters of its migration in soil-vegetative complex. Selenium and ferric, aluminium humate or hydroxide interactions play some special role.

5. Thus, the Se-deficiency is connected with geological, climatic factors and intensive land use.

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Докладът е рецензиран.