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Geochemical differentiation of iodine and selenium in landscapes: first results on example of the Bryansk region

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Introduction. A study of iodine and selenium in landscapes of the Bryansk region was started to estimate contribution of the natural background of these elements essential for thyroid gland [*Arthur et al*., 1999; *Ermakov*, 2004], to spatial distribution of thyroid diseases after contamination of the area by the Chernobyl radioiodine isotopes.

The Bryansk region is noted for a variety of the soil-forming rocks and soils [*Prosyannikov*, 2002], a pronounced deficiency of iodine in local diets [*Proshin, Doroshchenko*, 2005] which contributed to the risk of thyroid cancer in the region contaminated due to the Chernobyl accident [*Shakhtarin et al*., 2003]. At the same time an increase of the thyroid cancer in areas with different radiogenic load is comparable that could be a result of different reaction to radioiodine impact due to variation of stable iodine and selenium background.

The main objective of experimental work presented in this paper was to evaluate natural variation of selenium and iodine concentration in the components of the local food chain noted for I and Se sink (the soils) and transfer (drinking waters, plants).

Study region and methods

Selection of the test sites and sampling. Landscapes and soils of the Bryansk region are characterized by different geochemical features. Figure 1 presents a schematic map of landscapes different in soil and vegetation cover and in the dominating pH-Eh types of water migration according to Perelman (1975).

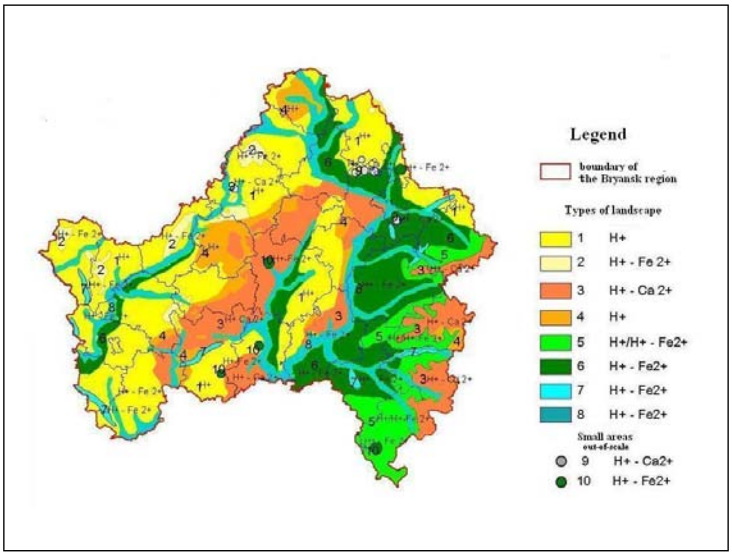

Figure 1. A schematic map of geochemical landscapes Обзорная of the Bryansk region (created by Korobova E. and Beryozkin V. on the basis of thematic maps of the Bryansk oblast' and the corresponding sheet of the State soil map, scale 1: 1000 000)

Landscape groups: 1, 2 – watersheds in areas of fluvio- and limnoglacial sands and sandy loams sand coniferous and mixed woodlands on podzolic and soddy-podzolic soils and agricultural lands; 3, 4 - watersheds in areas of covering and loess-like loams, primary oak and secondary birch and poplar forests on grey forest soils and agricultural lands; 5, 6 – ancient terraces and draining hollows in areas of: 5 – sandy and loamy deposits underlain by carbonate sedimentary rocks covered by oak forests and secondary broad- and small-leaf forests on light grey and grey forest soils including cultivated lands; 6 – sandy and loamy sand ancient alluvial, lacustrine, fluvioglacial deposits covered by pine and pine-spruce forests on soddy-podzolic soils and agricultural lands; 7,8 – modern flood plains and river terraces in areas of: 7 – reworked sandy limno-glacial deposits with domination of marshy meadows and peat bogs including meliorated areas used for grazing and haying; 8 – modern and ancient alluvial deposits of various texture, meadows and marshes used for grazing and haying; 9 – out-of-scale small areas of broad-leaf forests and meadows on soddy carbonate soils on outcrops of marls and limestone; 10 – out-of scale areas of marshy woodlands and meadows on soddy-gley, humus-gley soils located on watersheds and terraces. Classes of water migration (after Perelman, 1975): H^+ - acid; H^+ - Fe^{2+} - acid gley; H^+-Ca^{2+} - transitional to calcium (weakly alkaline); Ca^{2+}- Fe^{2+} - calcium-gley (locally).

The two most geochemically different landscape types situated in areas of fluvioglacial and moraine sandy and loamy sand sediments with mainly H^+; H^+ - Fe^{2+} classes of the soil water migration (polesje and moraine landscapes) and the areas of covering and loess-like loamy deposits the presumably H^+-Ca^{2+}, Ca^{2+}- Fe^{2+} soil water migration class (opolje landscapes) were selected for location of the test sites. To provide spatial proximity of the geochemical and medical date sampling was also carried out close to (pasture areas) or within (private farms) the settlements with statistical data on thyroid gland diseases and iodine renal excretion [*Proshin, Doroshchenko*, 2005]. In 2010 ten settlements (30 private farms) were examined. At the pastures the soils were sampled with the help of an auger to the depth of 20-30 cm with the further core slicing in increments of 5-10 cm. Plants were cut over the soil sampling area of 30x30 cm (50x50 cm in case of rare cover or damaged by cattle). Soil samples were stored in plastic bags. Plants were air-dried. Water samples were kept in a freezer isolated from air.

Laboratory analysis. Soil samples were analyzed for iodine without drying, the results were recalculated for the air dry basis to compare with the published data. Plants were milled using grain mill and ZM200 (Retsch, Germany). Iodine determination in water samples was performed without pre-concentration. Iodine was determined with the help of kinetic rodanide-nitrite method [*Proskuryakova, Nikitina,* 1976] using photometer KFK-3-01 (Russia). Iodine detection limit in solution was within 1-4 mg/ml, reproducibility varied from 7- to 20%. Se was determined in air-dry soil and plant samples by spectrofluorimeter [*Ermakov*, 1987]. Se detection limit equaled 1 ng/ml, reproducibility (according to plant standards) was up to 7%.

Results and their discussion. Se supply of drinking waters varied within two orders (0,02-4,4 µg/l) and corresponded to the general level characteristic for the natural waters (<1 µg/l, Plants et al., 2004). Se concentration in the upper humus horizons of the areas used for pasturing (0-5 cm, n=20) varied from the deficiency (0,07 mg/kg) to the relative normal level (0,95 mg/kg). However in plant samples (n=29) the Se content did not exceed deficiency level for forages (0,02-0,1 mg/kg dw) (Table 1).

Table 1. Se concentration in source components of the biogeochemical food chain in different landscapes

Object	Type of landscape	Number of samples	Parameters of Se concentration						
			units	min	max	mean	std*	Ge.	Me
Topsoil (0-5 cm, pastures)	Polesje and moraine	14	mg/kg dw	0,070	0,950	0,301	0,215	0,250	0,239
	Opolje	6	mg/kg dw	0,110	0,510	0,261	0,154	0,227	0,213
Grasses (pastures)	Polesje and moraine	15	mg/kg dw	0,021	0,079	0,044	0,018	0,041	0,038
	Opolje	14	mg/kg dw	0,024	0,100	0,056	0,026	0,050	0,060
Drinking water	Polesje and moraine	8	µg/l	0,02	0,40	0,14	0,15	0,07	0,06
	Opolje	17	µg/l	0,02	4,40	0,81	1,05	0,41	0,40

*standard deviation

The upper horizons of the grey forest soils developed in oplje landscapes and those of the soddy-podzolic soils collected in pasture areas of polesje and moraine landscape did not practically differ in Se content. Its mean value for the first group of samples was even lower than for the second. Nevertheless the content of Se in forage grasses sampled in opolje landscapes was pronouncedly higher as compared to those of the polesje and moraine areas (0,038 and 0,60 1 mg/kg correspondingly). This indicates that in areas used for pasturing in polesje and moraine areas Se may be less available to the plants. This was likely to result from water logging which was widespread within these areas and probably contributed to Se fixation in soils. In weakly alkaline oxygenic conditions typical for the opolje soils Se is known to be more mobile which could contribute to its availability to plants. Probably for the same reason drinking waters (mainly tap water) collected in the opolje settlements were characterized by a higher Se content as compared to those located within the polesje and moraine landscapes (0,06 и 0,4 µg/l, median values). Negative correlation between Se concentration in topsoil (0-5 cm) and grasses of the wet meadows also witnessed the low Se transfer to plants in water-logged conditions (Figure 2).

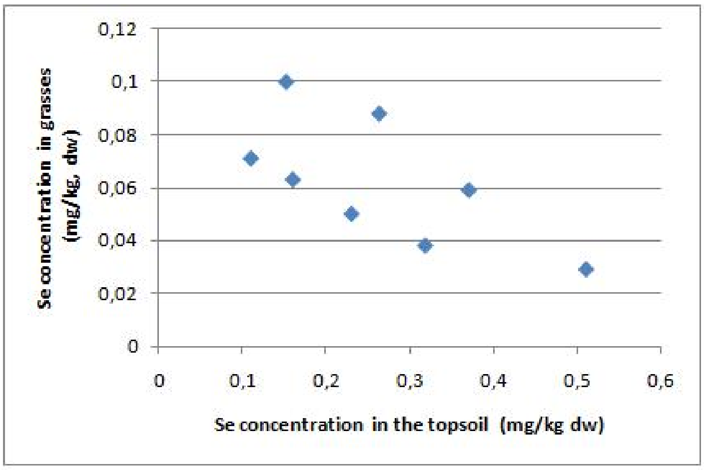

Figure 2. Relation between Se content in the upper soil horizon of wet meadows used for pasturing and the grasses growing above.

Unlike Se the minimum and mean estimates of I concentration in the same samples was considerably higher in soils and plants of the opolje landscapes as compared to those of the polesje and moraine. This proved a higher iodine status of the former landscapes (Table 2). Mean I concentration in the upper soil horizons of the polesje and moraine landscapes equaled to 2,1 mg/kg dw that corresponds to the lower threshold concentration established for soils (<2-Kovalsky, 1974) In the opolje topsoils the mean I content exceeded this threshold (3,21 mg/kg dw). Maximum I values were characteristic for topsoil layers of wet meadows located in subordinated landscapes (up to 15 mg/kg). I concentration in plants of the pastures varied from 0,08 to 0,72 mg/kg (Table 2).

Similar to I in topsoil the amount of I in forage grasses collected in the opolje landscapes was higher than in the polesje and moraine areas (Table 2) but exceeded the lower threshold of the optimal interval for cattle rations (< 0,07 mg/kg dw, Kovalsky, 1974) in all the regions. The reason for this needs further investigation.

Table 2. I concentration in source components of the biogeochemical food chain in different landscapes

Object	Type of landscape	Number of samples	Parameters of I concentration						
			units	min	max	mean	std*	Ge.	Me
Topsoil (0-5 cm, pastures)	Polesje and moraine	11	mg/kg dw	0,37	15,8	2,09	4,57	0,89	0,75
	Opolje	11	mg/kg dw	0,77	15,5	3,21	4,49	1,84	1,32
Grasses (pastures)	Polesje and moraine	16	mg/kg dw	0,08	0,72	0,33	0,23	0,25	0,25
	Opolje	14	mg/kg dw	0,18	0,63	0,38	0,16	0,35	0,36
Drinking water	Polesje and moraine	14	µg/l	1,28	25,1	10,2	6,1	8,33	9,20
	Opolje	21	µg/l	0,70	23,5	5,95	5,64	4,06	3,65

*standard deviation

Analysis of I and Se transfer to plants for the topsoil (transfer coefficients, TC, weight basis) proved that on the average I uptake by plants is relatively higher than Se (0,55±0,06, n=22 and 0,22±0,05, n=16 respectively). When the type of landscape was considered, it appeared that Se uptake by plants at the test plots located in the polesje and moraine landscapes was lower than I (TC_{Se} 0,29±0,09 and TC_I=0,72±0,14, n=6). At four test plots situated in opolje landscapes Se uptake by plants was in two cases higher in one case –equal and in one –lower than that of I that lead to a slightly higher median of TC_{Se} value as compared to TC_I (0,44 and 0.38 correspondingly). Obtained results showed different behavior of Se and I in soils and their transfer to grasses in similar landscape geochemical conditions.

Iodine concentration in drinking water collected in areas of polesje and moraine landscapes was generally higher than in the opolje landscapes. This may result from a higher mobilization of I in the iodide form in the reduced environments typical for the former group of landscapes. In opolje areas I may be fixed in soils and sediments on carbonate oxidizing barrier.

Therefore the difference in I and Se behavior was likely to reflect different chemistry of elements, as well as pH and redox conditions dominating in the two groups of landscapes. Further studies are necessary to verify the observed tendencies.

Conclusion

1. First experimental data to characterize I and Se behavior in geochemically different landscapes were obtained.

2. Iodine and selenium concentration and distribution in topsoil, grasses and drinking water appeared to be different within areas of landscapes formed on fluvioglacial and moraine deposits (polesje and moraine) and on the covering loess-like loams (opolje).

3. Forage grasses of the opolje landscapes were proved to contain a higher amount of I and Se as compared to those of the polesje and moraine. However topsoil and drinking water in particular collected in the former landscape type had lower Se content as opposed to I which concentration was higher in these objects within the polesje and moraine group of landscapes.

4. Selenium uptake by plants appeared to be relatively lower as compared to iodine uptake particularly in areas of the polesje and moraine landscapes.

5. The difference in I and Se behavior was suggested to result from different chemistry of elements and the pH and redox conditions dominating in the two groups of landscapes.

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