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Distribution and speciation of iodine in drinking waters from geochemically different areas of Bryansk region contaminated after the Chernobyl accident in relation to health and remediation aspects

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ABSTRACT

Chemical composition of drinking water from different sources was studied in private farms distributed in areas of the Bryansk region contaminated by radionuclides after the Chernobyl accident. Concentration of major ions showed clear relation to water-bearing rocks and local anthropogenic contamination (e.g. N, P). Drinking water was in general impoverished in I (Me = 5.76 μg/l that is below the lower limit of sanitary standard equal to 10 μg/l). Thermodynamic modeling based on chemical composition of the samples showed that the predominant form of iodine is iodide and it forms mineral complexes CaI^+, CaI_2, MgI^+, MgI_2, etc. that explains iodine concentration on carbonate barrier in soils and rocks. Complexes' formation may have contributed to radioiodine retention in water during its fallout with further natural decontamination of aqueous phase during water filtration through soils and sediments enriched in carbonates and organic matter. Comparison with distribution of thyroid cancer cases among rural population revealed a tendency of the inverse relation between the number of cases and iodine content in dug well waters; the finding needs further investigation.

1. Introduction

The Chernobyl accident that took place on April 26th 1986 has led to a considerable contamination of vast areas with technogenic radionuclides including radioiodine isotopes registered all over the world in aerial fallout, grass and milk (Skutskar, Sweden (Krey et al., 1986): Thessaloniki, Greece (Papastefanou et al., 1988), Chester and Spokane, USA (Dreicer and Klusek, 1988; Pickett, 1987) correspondingly). The highest activity of ^{131}I was found in size fractions smaller than those for the nuclides ^{137}Cs, ^{132}Te and ^{103}Ru (Baltensperger et al., 1987). According to (Seki et al., 1988) iodide was the predominant species; no iodate was noted on 1–6 May; in the mid-May sampling period the iodate concentration was 1/3 that of iodide and by June 1, ^{131}I species were not detectable.

Although short-living, the radioiodine isotopes which entered mammals' bodies through inhalation and the direct food chain soil-grass-milk/soil-potato) were accumulated by thyroid gland as a target organ and caused its irradiation increasing the risk of thyroid cancer among children as the most sensitive cohort among population of the regions subjected to radionuclide fallout. Stable iodine deficiency in organisms that was proved by its low concentration in the urine or soil cover was the additional factor contributing to health risk (Cardis et al., 2005; Shakhtarin et al., 2003; Korobova et al., 2014).

The main source of iodine in the human diet is food of plant origin. It is considered that the contribution of drinking water to total intake of the trace element is not more than 5–10% (Sukhinina et al., 1995; Fuge, 2005). Meanwhile there are evidences of a close connection between the chemical composition of drinking waters and the prevalence of endemic diseases among its consumers (Gurevich, 1968; Karpova, 1957). In some cases the water factor plays a crucial role (Charhinets, 1992; Chidiogo and Azuka, 2013). In addition, the level of iodine in natural water can be used in the comprehensive assessment of the status of the territories characterized by the lack of this trace element (Chidiogo and Azuka, 2013; Schumm-Draeger, 2004).

Forms of migration of iodine and geochemical conditions of environment determine the ability of the trace element for migration and concentration on geochemical barriers. Iodine exits in natural water as iodide and iodate ions. Under certain conditions, the halogen may be present in molecular or methylated forms (Vernadskij, 1967; Vinogradov, 1927, and others). There are data on prevalence of organic complexes with iodine in case of water enrichment in dissolved organic matter (Kaplan et al., 2000). In addition, correlation between I content in drilled wells of the of the private farms and in the milk produced in

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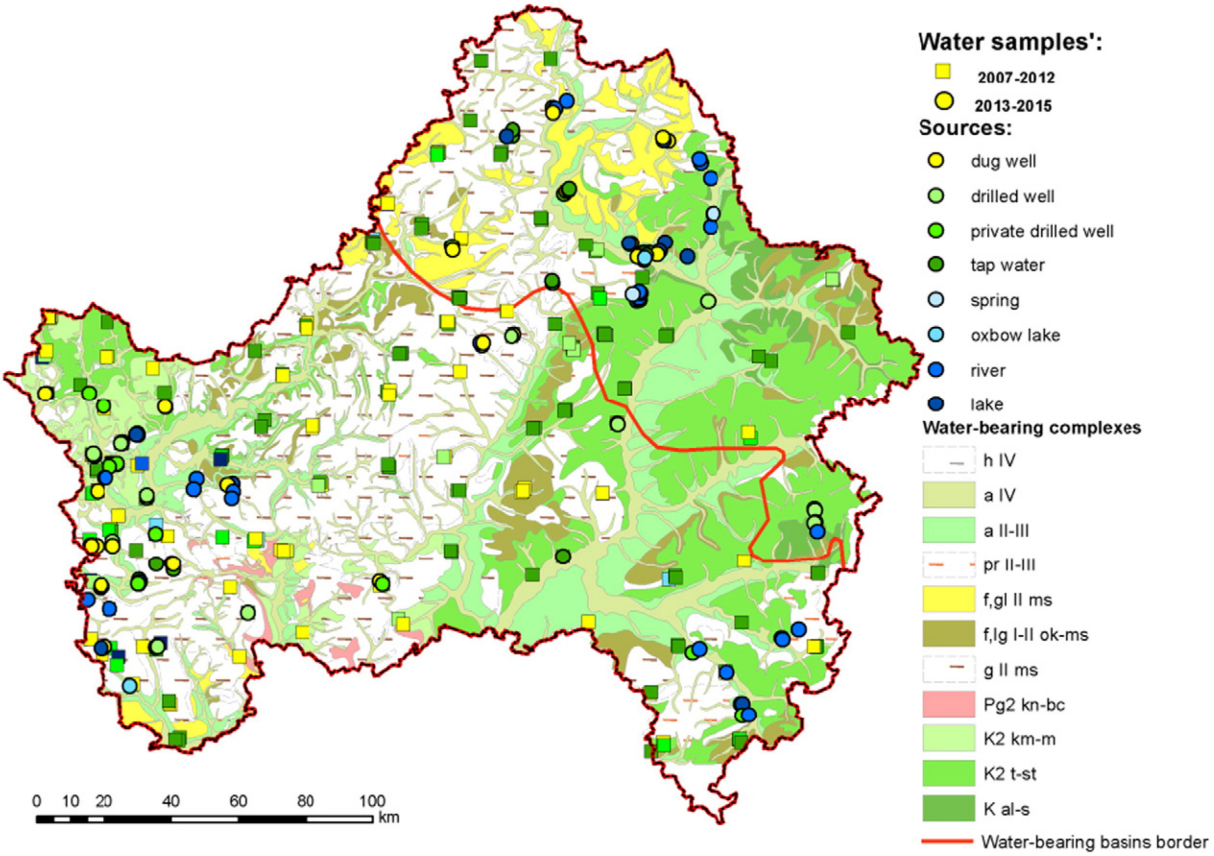

Fig. 1. Distribution of water samples collected from different sources in 2005–2012 (squares) and in 2013–2015 (circles) on the hydrogeological map of the Bryansk region.

these farms found earlier (Korobova et al., 2014) showed that water may be significant in I supply of local rations and diets. Accounting of water content in vegetables and fruit produced in situ one may suggest at least twice as much water contribution in iodine supply of local rural diets (i.e. ca 20–24%). Iodine is known to be an active aerial and water migrant (Perel'man, 1975) and bioavailability of both stable and radioactive iodine isotopes and specificity of their uptake by living organisms largely depend upon geochemical parameters of the environment and its water migration. We infer that a presence of radioactive isotopes of iodine in the environment in conditions of its natural deficiency may significantly increase the risk of specific diseases of the thyroid gland, and on the contrary, higher iodine content in drinking water may have played a protective role in the period of radioiodine fallout.

The main aim of the investigation was to study and evaluate water composition, stable iodine supply and its migration forms in different geochemical conditions typical for the areas of Bryansk region contaminated by radioactive iodine isotopes after the Chernobyl accident in relation to decontamination and health issues.

2. Study area

The Bryansk region belongs to areas with low iodine content in the environment due to its inland location (Koval'skij, 1974; Proshin and Doroshenko, 2005). Variety of rocks, sediments and soils (Prosyannikov, 2002) defines significant geochemical variety of landscapes and the corresponding classes of water migration of chemical elements according to Perelman (Perel'man, 1975). The two most geochemically different types of landscapes correspond to lowlands formed on mostly sandy fluvioglacial deposits with acidic (H) and acid-ferruginous (H-Fe) classes of water migration (polesje landscapes) and the elevated areas of loess-like loamy sediments often enriched in carbonates with calcium (Ca) and transitional acid-calcium (H-Ca) classes of water migration (opolje landscapes).

According to hydrological and geological data the most contaminated South-Western part of the region is a part of the Dnieper basin (Antipov et al., 2001) where the upper strata of aquifer complexes are presented by Quaternary, Neogene, Paleogene and locally Cretaceous rocks. The lower level is formed of complexes of the Paleozoic and the Archean-Proterozoic sediments. The centralized water supply is provided by waters collected over the Upper Cretaceous aquifers and is noted for bicarbonate-calcium and sulphate-hydrocarbonate magnesium-calcium composition with a salinity ranging within 190–750 mg/l. Centralized drinking water supply of the North-Eastern part of the region is formed within Moscow basin over the Paleozoic (upper Devonian) aquifer. The composition of water is predominantly

Table 1
Chemical composition of the collected drinking water samples (statistical data).

Water pH, salinity and major ion concentration, units	Statistical parameters								
	n	Min	Max	Mean	std	V, %	Me	Ge	Mo
Ca″”, mg/l	471	0,133	588	88,5	59,5	67	81,4	72,7	108,0
Mg″”, mg/l	471	0,8	140	13,8	12,5	91	10,0	10,0	4,6
K′’, mg/l	462	0,18	370	14,5	28,5	197	6,0	6,2	0,9
Na′’, mg/l	471	0,46	519	17,6	39,6	225	6,4	8,1	4,1
HCO$_3$’′, mg/l	436	4,3	946	279,5	147,0	53	274,5	231,2	396,5
Cl′’, mg/l	441	1,07	742	32,6	62,0	190	13,1	15,4	8,9
SO$_4$″, mg/l	441	0,19	2230	38,4	133,0	347	15,9	14,4	16,8
NO$_3$’′, mg/l	441	0,12	502	18,8	46,3	246	6,2	6,8	2,5
PO$_4$’″′, mg/l	405	0,009	45	1,7	4,3	255	0,4	0,5	0,3
pH	437	4,72	9	7,4	0,6	8	7,5	7,4	7,8
Salinity, mg/l	474	5535	4757	482,7	383,3	79	421,8	379,5	nd

Table 2
Concentration of chemical elements in drinking water samples.

Chemical elements, units	Statistical parameters								
	n	Min	Max	Mean	std	V, %	Me	Ge	Mo
Fe, mg/l	401	0,0025	20,7	0,644	1865	290	0,175	0,159	0,009
Mn, mg/l	388	0,0008	1,97	0,122	0,203	167	0,05	0,043	0,05
Al, mg/l	261	0,0007	4,54	0,158	0,353	223	0,013	0,021	0,0009
Si, mg/l	195	0,12	22,02	7,65	4,78	63	7,63	5374	13,1
Sr, mg/l	459	0,007	12,4	0,620	1213	196	0,35	0,379	0,29
Ba, mg/l	232	0,0006	1,07	0,057	0,106	187	0,0306	0,028	0,01
Cu, mg/l	194	0,0009	4,64	0,466	1210	260	0,0013	0,009	0,0009
Zn, mg/l	298	0,001	3,66	0,091	0,273	300	0,023	0,015	0,001
Co, mg/l	242	0,0009	0,625	0,070	0,167	240	0,0009	0,003	0,0009
Ni, mg/l	242	0,0009	0,363	0,049	0,107	218	0,0009	0,003	0,0009
Cr, mg/l	200	0,0005	1,18	0,182	0,336	185	0,0009	0,007	0,0009
F, mg/l	425	0,004	4,18	0,334	0,343	103	0,23	0,233	0,15
I″, µg/l	495	0,068	50,14	7,94	7141	90	5,76	5733	0,6
I″ after filtration (<0,45 um), µg/l	95	0,595	35,12	7,87	6354	81	5,61	6282	3,44
mg O_2/l	81	0,17	120,28	22,17	28,62	129	10,54	11,150	6,11

of calcium bicarbonate, calcium-magnesium and sodium-calcium. The salinity of the centralized water varies from 200 to 800 mg/l. However local population is widely using water from private bore holes 10–15 m deep and open wells draining the uppermost ground water. Composition of these sources were expected to be closer related to the local geochemical conditions of the soil and its parent rock.

2.1. Methods

Samples of surface and drinking water were collected at the end of July and beginning of August of 2005–2015 close to or in rural settlements including private farms where data on medical examination was available. Samples characterized the dominating water sources: artesian, non-artesian drilled or dug wells (Fig. 1). In situ measurements included water pH, Eh and conductivity. To exclude fast sorption a portion of sampled water (100 ml) was immediately acidified with HNO_3 (1:100). Determination of chemical elements was performed with the help of modernized ICAP9000 polychromator and ICP AES AA Perkin Elmer 603 (K).

Major anions were determined by selective electrodes and potentiometric titration, bichromate oxidation was used for the organic carbon determination, kinetic rhodanide–nitrite techniques - for iodine (iodide ion, Proskuryakova and Nikitina, 1976). The detection limit for I equaled to 1 ng/ml, the accuracy did not exceed 2–7%.

Thermodynamic modeling of iodine occurrence forms in the water-rock system was carried out using software HCh, developed by Yu. V. Shvarov, MSU; database Unitherm, Department of Geochemistry, Moscow State University. The simulation is based on the calculation of the equilibrium composition of a chemical system by minimizing its Gibbs free energy at the given temperature, pressure, and bulk system composition (Shvarov, 2015). The applied system consisted of 19 independent elements (Ca, Sr, Mg, Na, K, Al, Fe, Si, C, O, H, N, S, Se, P, F, Cl, I, Zn) and was open for oxygen and carbon dioxide. The simulated system contained an aqueous solution (127 ions and complexes) and 12 solid phases including sorbents typical for the studied soils (goethite and pyrolusite, sorption constants were taken from Li and von Gunten (1988). Calculation was performed for standard conditions of 10 °C and 1 bar.

3. Results

3.1. Chemical composition of water samples

Collected samples were characterized by low salinity (0.483 g/l on the average, except for one artesian balneary source 200 m deep – 4,7 g/l) and the dominating hydrocarbonate-calcium composition (Table 1). Concentration of nitrates and phosphates was also rather low (mean value equaled 18,8 and 1,7 mg/l correspondingly). High variation coefficient was due to maximum values (502 and 45 mg/l) that characterized local contamination of the individual shallow wells.

Content of the other macro- and microelements in the collected samples in general meets the state sanitary requirements (State inspection rules 2.1.5.1315-03), except for a few samples (Table 2).

In 77% of water samples I content did not exceed 10 µg/l (7.5 µg/l on the average, median value – 5.3 µg/l, Fig. 2) that is below its lower physiological level accepted for drinking water (10–125 µg/l).

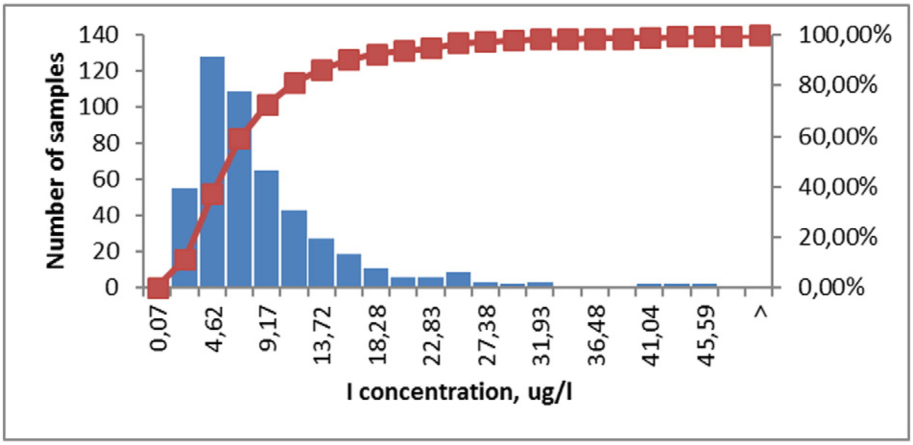

Fig. 2. Distribution of I in drinking water samples.

Table 3
Iodine in waters collected from different sources in areas with different classes of water migration (μg/l, 2007–2012, Korobova et al., 2014).

Type of water	Landscape type with characteristic classes of water migration*	n	Min	Max	Mean	std	V, %	Ge	Me
Centralized water supply from a single drilled well (water pipe)	1*	67	0,60	25,1	6,79	5,76	85	4,96	4,54
	2	52	0,88	40,7	6,66	5,96	90	5,20	5,41
Private standpipes, drilled wells	1	11	0,84	18,9	5,38	5,74	107	3,36	2,60
	2	16	0,70	40,1	9,81	10,7	110	5,72	5,18
Dug wells and springlets	1	64	0,60	30,0	7,28	5,70	78	5,63	5,28
	2	18	1,80	34,3	13,2	9,02	69	10,4	9,93

*1 - polesje and moraine landscapes: H^+ (autonomous acid), H^+-Fe^{2+} (subordinate acid-gley) class of water migration; 2 - opolje landscapes: H^+-Ca^{2+}, Ca^{2+} (autonomous transitional and calcium), H^+-Ca^{2+}-Fe^{2+}, Ca^{2+}-Fe^{2+} (subordinate transitional and calcium-gley) class of water migration (Korobova et al., 2014), Water migration classes after Perel'man (1975).

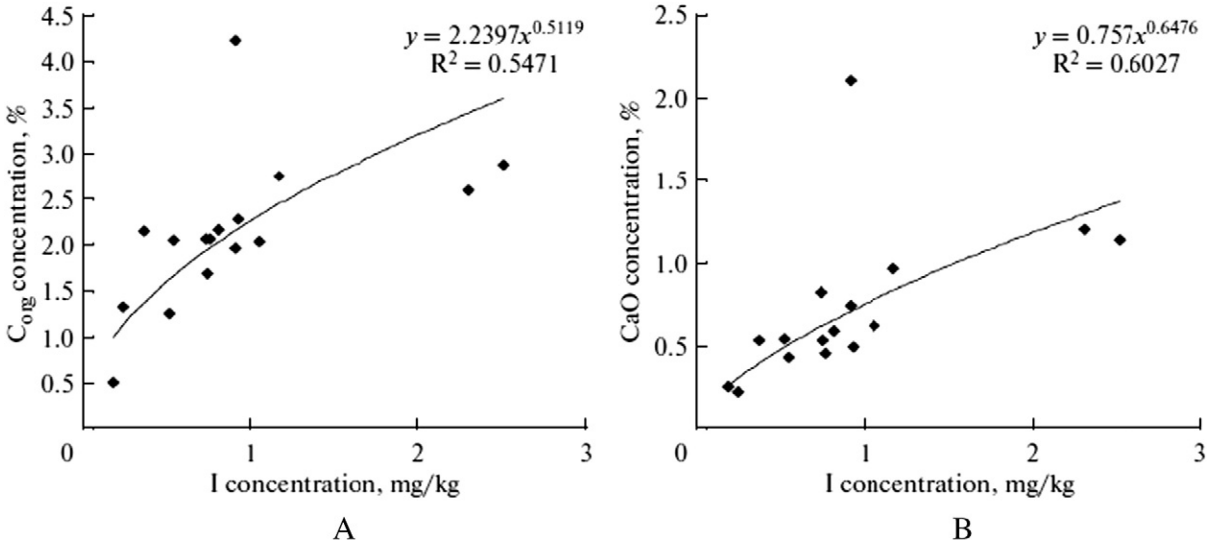

Fig. 3. Dependence of I concentration in soil upon the content of carbon (A) and calcium (B, Korobova et al., 2014).

Despite high variation of I in all water types (Fig. 2) the water from dug wells showed a comparatively higher I concentration as compared to other sources feeding on deeper water-bearing layers (except for the already mentioned case of balneary artesian source). According to the data of 2005–2012 I content in drinking waters from private drilled and dug wells in opolje landscapes was twice higher as compared to polesje and moraine areas (Table 3). This could be due to higher I concentration in the upper soil horizons, where I content correlated with the amount of organic carbon (C) and calcium (CaO, Fig. 3).

In centralized sources sampled in 2007–2012 I content was almost similar irrespective to landscape type (Table 3).

3.2. Thermodynamic estimation of trace elements' speciation in water samples

Thermodynamic modeling based on the measured chemical composition of the samples was performed for 50 samples of water. It showed that the dominating aqueous forms were as follows: H_2O, H^+, OH^-, H_2, CO_3^{2-}, HCO_3^-, CO_2, Ca^{2+}, $CaOH^+$, CaF^+, $CaCl^+$, $CaSO_4$,$CaHSO_4^+$, $CaHPO_4$, $CaH_2PO_4^+$, $CaCO_3$, $CaHCO_3^+$, $Ca(HCO_3)_2$, Cl^-, HCl, F^-, HF, HF_2^-, $FeOH^+$, $Fe(OH)_2$, $Fe(OH)_3^-$, $FeCl^+$, $FeHSO_4^+$. The corresponding equilibrium solid phases were presented by calcite, dolomite, quartz, apatite, ankerite, and in some cases by strontianite and saponite-Ca (Table 4). All the

Table 4
Calculated deposited solid phases in some samples (for all samples $lgPO_2$ (bar) = −63).

Sample index	Source type	$lgPCO_2$ (bar)	pH	Eh (V)	Dominant mineral phases
Kozh-1	Drilled well	−6	9,7	−0,18	Apatite-F, dolomite, chlorite
Dem-2	River	−2,4	7,6	−0,12	Apatite-F, calcite, quarts, stilbite
Rog-1	Dug well	−0,9	6,6	−0,02	Apatite-OH, quarts, ankerite, stilbite
Rog-3	Lake	−2,1	7,3	−0,11	Apatite-F, kaolinite
Gla-2	Dug well	−0,5	5,5	0,05	Quarts, apatite-F, kaolinite
Glo-1	River	−1,4	6,9	−0,09	Calcite, dolomite, quarts, ankerite
Ivot-2	Tap water	−1,6	7,1	−0,04	Strontianite, quarts, ankerite, stilbite, apatite-F
Tit-2	River	−0,9	6,2	−0,05	Apatite-F, quarts, stilbite,
Ugr-1	Drilled well	−4,6	9,1	−0,15	Quarts, chlorite, dolomite, apatite-F, strontianite, saponite-Ca
Gla-1	Lake	−2,7	7,6	−0,13	Kaolinite, apatite-F
Sel-3	Dug well	−0,4	5,8	0,03	Quarts, kaolinite, apatite-F
Zam-2	Drilled well	−1,4	6,7	−0,02	Quarts, siderite, apatite-F, stilbite
Klin-1	Lake	−2,9	7,9	−0,15	Calcite, dolomite, apatite-F, apatite-OH, quarts, stilbite

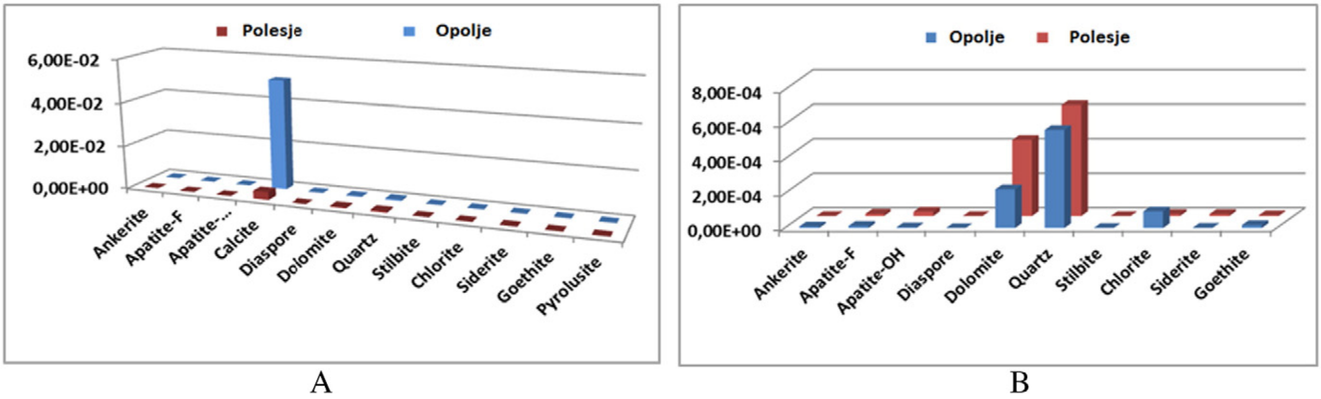

Fig. 4. Calculated solid phase composition and amounts of phases (mol/kg): A – calcite phase included, B – without calcite phase.

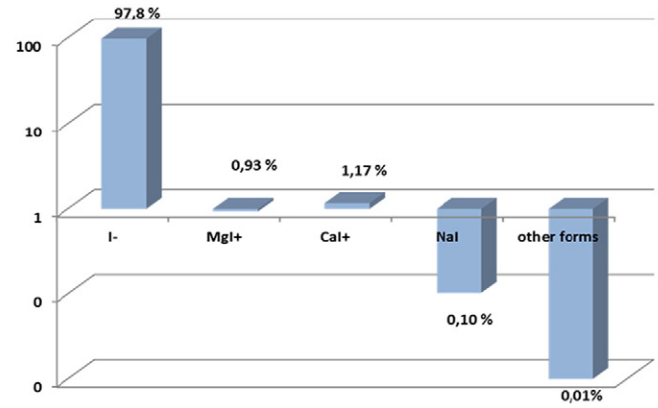

Fig. 5. Calculated speciation of iodine in studies water samples.

analyzed water appeared supersaturated with respect to calcite, quarts and dolomite (Fig. 4).

Table 4. A fragment of the results of thermodynamic modeling speciation of chemical elements in aqueous and solid phases.

The presence of calcite in solid phase appeared to be crucial for both geochemical landscapes and opolje in particular where its domination was obvious while in absence of the calcite phase (not included), the main solid phases were presented by quarts and dolomite, and quartz amount was naturally higher in polesie landscapes (Fig. 4, Kolmykova et al., 2016).

According to modeling the main iodine species in aqueous phase in all cases was iodide with a minor contribution of its mineral complexes with Ca and Mg (Fig. 5). Modeling with the new data confirmed previous finding that these complexes exhibit good correlation with total iodide (Korobova et al., 2014) that means that at higher concentration of Ca and Mg ions more iodine is bound and may be fixed during water migration in soils and sediments on carbonate geochemical barrier. The latter fixation has been observed in vertical profiles of the leached grey forest and soddy-carbonate soils (Korobova, 1992; Korobova et al., 2014). We hypothesize that iodide deposition on calcium-carbonate geochemical barrier may take place due to destruction of CaI^+ with deposition of $CaCO_3$ and release and sorption of iodine.

In this study we also evaluated concentration of goetite and pyrolusite as possible iodine sorbents. The possibility of iodine fixation by iron hydroxides was discussed earlier by Fuge and Johnson (1986). Equilibrium content of pyrolusite appeared to be insignificant while that of goetite was considerable especially in tap water where its concentration may be an order higher than in ground water from the dug wells (Fig. 6, A). This phase showed a rather high affinity to iodide (Fig. 6, B). This means that drinking water with high goetite content that is the case of tap water and ground water in subordinated polesje landscapes (H^+-Fe^{2+} class of water migration) will be particularly impoverished in iodide.

This conclusion was supported by statistical calculation performed for iodine from the selected groups of different water sources collected in areas with acid (H^+ watershed polesje landscapes with soddy-podzolic soils), acid-gley (H^+-Fe^{2+} subordinated polesje landscapes with meadow gley soils) and transitional acid-calcium (H^+-Ca^{2+}, watershed

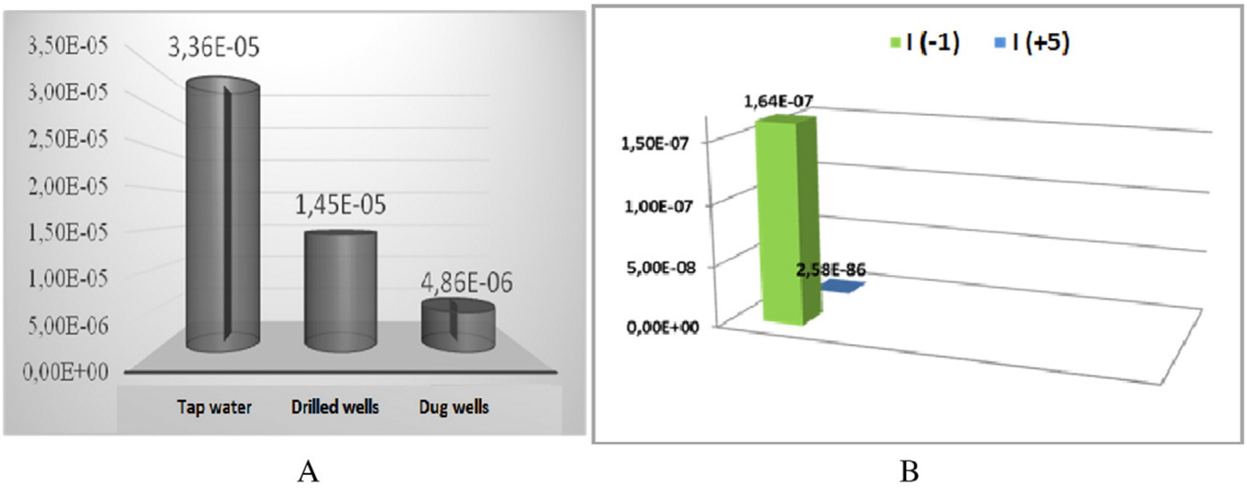

Fig. 6. Content of goethite in different types of drinking waters (A, mol/kg) and thermodynamic evaluation of its sorption of iodide and iodate (B, mol/kg).

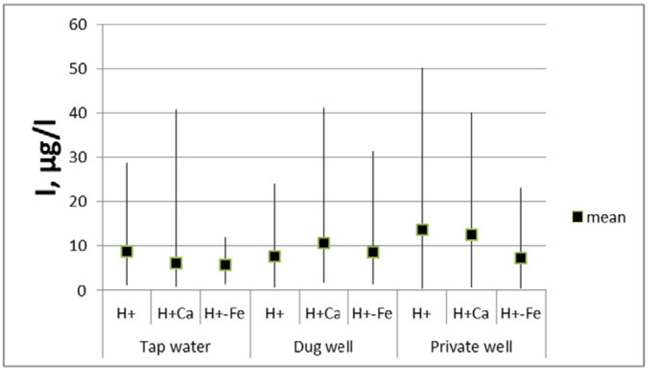

Fig. 7. Variation of iodide content in waters from different sources within the areas with domination of different classes of water migration (number of samples equaled to: tap water – 29, 41 and 12; dug well water – 24, 41 and 31; private drill wells – 50, 40 and 23).

opolje landscapes with leached grey soils) classes of water migration (Fig. 7).

Despite of a wide variation the mean iodide value was comparatively low in tap water and reached maximum in water from private wells and dug wells in opolje landscapes.

A tendency of lower papillary thyroid cancer cases in rural settlements with higher iodine content in dug wells was found within every of four zones with different correlation between the number of cancer cases and radioiodine attack found earlier (Korobova, 2016; Fig. 8). This means that there exists possibility that drinking water from the dug wells used during the accident may have contributed to decrease of negative health effect among rural population.

4. Conclusion

Drinking water from different sources used in private farms distributed in areas of the Bryansk region contaminated by radionuclides after the Chernobyl accident are of generally low salinity and hydrocarbonate-calcium composition. Concentration of major ions showed clear relation to water-bearing rocks and local anthropogenic contamination (e.g. N, P). Drinking water was in general impoverished in I (Me = 7,5 µg/l that is below the lower limit of sanitary standard equal to 10 µg/l).

Thermodynamic modeling based on chemical composition of the samples helped to establish equilibrium occurrence forms of chemical elements and showed that the predominant form of iodine in local drinking water is iodide, the latter forming mineral complexes CaI^+, CaI_2, MgI^+, MgI_2, etc. Therefore, on one hand, iodine complexation may have contributed to radioiodine retention in water during its fallout, but on the other hand filtration of contaminated water through soils and sediments enriched in carbonates and organic matter leads to radioiodine fixation, thus showing the way of natural decontamination of drinking water.

A tendency of inverse relation between the number of thyroid cancer cases among rural population and iodine content in dug well waters was revealed in different radioiodine contamination zones that needs further deeper investigation.

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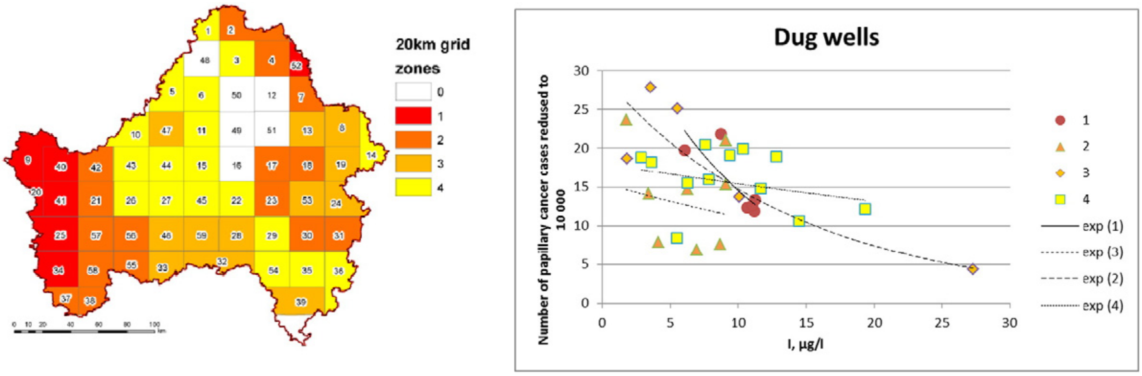

Fig. 8. Grid zones with different correlation between the number of papillary cancer cases of thyroid in the period of 1986–2009 and ^{131}I fallout estimated on the basis of ^{137}Cs contamination and a tendency of relation between the number of cases and stable iodine in dug wells in these zones (only rural settlements are considered, blank zone was excluded from consideration due to arrival of residents from the contaminated zones; the cell number 9 was excluded from zone 1 due to low population).

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