Bromine and Iodine in Natural Waters of the South of West Siberia

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(Received February 30, 2003; in revised form August 26, 2003)

Abstract

The bromine and iodine content and distribution in the soils and natural waters of the south of West Siberia are studied. Questions associated with the pattern of accumulation and migration of halogens in the soil profile, and with the conditions in natural waters contributing to, or hindering the accumulation of halogens in them, are discussed.

INTRODUCTION

The necessity of iodine for a normal development of human and animal organisms has been known since very long [1–5]; studies have also been carried out whose results witness to a positive influence of this element on some plant species [6–8]. As for the bromine, despite its wide use in some branches of industry, remains up to the present time a poorly studied element. Only a few publications on studies of bromine in soils are known [4, 9, 10]. Nevertheless, recently, the halogens (fluorine, chlorine, bromine and iodine), together with such trace elements as manganese, copper, cobalt *etc.* [11], began to be considered as belonging to the group of elements having a strong influence for life, which, of course, raises some questions. For example, due to insufficient studies of bromine in various natural objects, it was impossible to conclude unequivocally about positive influence of this halogen on living organisms. There are publications witnessing to a negative effect of bromine in a complex with boron in water on human organism [12]. Moreover, the bromine is a toxic halogen and belongs to the group of elements of the second class of danger [13].

The goal of the present work is to generalize the materials obtained by us in the study of the total content, and of that of water-soluble forms of, bromine and iodine, and their concentration in natural waters l in the territory of the south of West Siberia [14–16]. Besides, an attempt was made to give a preliminary estimate of halogen content of these natural objects with respect to the criteria available today.

The results obtained on halogens in the soils of the territory studied, because of lack of state standards, will be compared with the threshold concentrations for the total iodine according to V. V. Kovalsky [1] in which the content of this element of less than 5 mg/kg of soil is qualified as insufficient, that within the range of 5–40 mg/kg of soil is considered as normal, and that of more than 40 mg/kg as excessive. Concentrations of water-soluble form of iodine will be interpreted on the basis of Yu. G. Pokatilov's gradations, according to which the ranges of 0.011–0.03, 0.03–0.05 and 0.05–0.1 mg/kg of soil correspond to a low, lowered, and optimal substance content, respectively [3]. Iodine content of natural waters will be estimated by means of its comparison with the norm (10 μg/l) recommended by endocrinologists for potable water [17].

As for the bromine, due to the absence of not only MPC, but of any other estimation criteria, it is not expedient to compare our results with any other data. This halogen content in various soil types may be established only at the qualitative level of "more – less". Bromine concentration in natural waters will be compared with its permissible concentration in potable water (0.2 mg/l), which is regulated according to SanPiN 2.1.4. 559–96.

HALOGENS IN SOILS

Soil samples were collected in the territory of Barabinsk, Kulunda, Vasyugan and Ishim plains, the Priobskoye plateau, and the Surgut lowland. Zonal soils are represented by soddy podzolic, grey forest, chernozem and chestnut soils; the interzonal ones are represented by solonchaks, solods and solonetzs.

The total and water-soluble iodine form content in soil specimens was estimated by means of kinetic rhodanide-nitrite method [19]. For estimation of water-soluble iodine, a water extract in the soil : water ratio of 1 : 4 according to [20].

The total bromine content was estimated using a combination of two techniques. The first part, including the transfer of the sample to solution, was carried out according to V. F. Kamenev [21], the second one was performed according to the classical Winkler's method described in [22]. The soil: water ratio in the aqueous extract for the assay of water-soluble bromine form was analogous to that used for iodine, with subsequent assay of the element according to Winkler. The soil humus content was estimated according to Tyurin in Nikitin's modification, pH was measured potentiometrically, the granulometric composition was estimated by the pyrophosphate method.

Soil samples from each cut were analyzed in three replications. The preparation of samples including drying, crushing and sifting was carried out by the technique generally accepted in pedological and agrochemical studies [23]. Specimens of natural (surface, ground and subterranean) waters were collected in the territory of the Baraba, Kulunda and Vasyugan plains. Iodine was assayed by the kinetic rhodanide-nitrite method [24], bromine was studied by Winkler's method. About 40 samples were analyzed. Analysis of water samples was carried out immediately after their supply. In cases of necessity, conservation and storage conditions were observed according to the demands of the method [25].

As the studies have demonstrated, the bromine and iodine content and distribution in the profile of the investigated soils by the complex of the soil and chemical properties of the given elements are determined. The influence of such a source of halogens as the sea and therefore the sea air, was not taken into account due to the considerable remoteness of the territory under study from the seawater areas.

The most important chemical properties of bromine and iodine capable of influencing their accumulation and migration in the soil profile include the high chemical activity of these halogens, the great mobility of bromide and iodide anions as compared to chloride, nitrate and carbonate anions [26], and the volatility of iodide, capacity of bromine to easily form vapors and the sufficiently good water solubility of the majority of salts of these elements.

The properties of soils exerting the strongest influence on the accumulation and migration of halogens in the soil profile include the degree of enrichment of the latter with organic substances, the granulometric composition, the medium reaction, the water regime and the presence of carbonates [2–10, 27, 28]. In other words, the accumulation and character of halogens distribution in various soil types depend on their genetic properties.

Various combinations of soil properties and manifestation, depending on this, of definite halogen properties result in manifold concentrations of halogens in the soil.

Let us consider the obtained data separately for each type of soil (Table 1).

Soddy podzolic soils of the Vasyugan plain

The evident absence of any symptoms contributing to accumulation of halogens in these soils has determined also the insignificant

TABLE 1

Some agrochemical indices of the main soil types in the south of West Siberia, and their iodine and bromine content

Cut number	Site of sample collection	Soil	Horizon	Depth, cm	Humus, %	pH of water	Iodine, mg/kg		Bromine, mg/kg	
							total	water-soluble	total	water-soluble
151	Surgut lowland	Deep-soddy deep-podzolic middle sandy loam	Ad	5–14	3.46	4.32	2.02	0.001	3.90	0.89
			A_1	14–25	0.93	4.30	2.30	0.004	2.81	0.43
			A_2	35–45	0.50	4.51	1.68	0.002	1.17	0.10
			BA_2	65–75	0.25	4.89	0.88	<0.001	1.00	<0.01
			A_2B	90–100	–	5.35	0.87	<0.001	1.15	<0.01
			B	150–160	–	5.70	1.12	–	1.40	0.15
			C	245–265	–	6.02	1.36	–	1.35	0.10
152	» »	The same	A_1	6–13	3.23	–	<0.01	–	2.61	0.67
			A_1	20–30	0.54	–	2.36	0.006	1.23	0.22
			A_1A_2	40–50	0.15	–	0.72	0.005	0.80	0.10
			A_2	60–70	0.017	–	0.23	<0.001	0.60	<0.01
			A_2B	130–140	–	–	0.24	<0.001	<0.03	<0.01
			C	180–200	–	–	Not detected	–	<0.03	<0.01
181	Vasyugan plain	Gray forest powerful heavy sandy loam	A_1	1–20	3.42	5.52	2.82	0.081	2.88	0.61
			A_1A_2	25–45	–	–	2.0	0.022	1.79	0.53
			A_2B	50–60	0.63	7.37	2.1	0.038	1.52	0.41
			B	70–80	–	–	–	–	–	–
			BC_k	90–100	1.06	8.19	3.15	0.090	3.12	1.00
			C_k	200–220	0.38	8.13	1.44	0.015	3.00	1.05
153	Ishim plain (western part)	Ordinary solonetzic shallow weakly humic middle sandy loamy chernozem	A_p	0–20	3.16	6.54	4.00	0.088	8.15	–
			B	50–60	0.32	7.75	3.76	0.057	4.46	–
			B_k	80–090	0.30	8.20	3.30	0.040	3.35	–
			BC_k	–	–	–	–	–	–	–
			C_k	140–150	0.15	8.24	1.36	0.020	2.95	–

Table 1 (continued)

Cut number	Site of sample collection	Soil	Horizon	Depth, sm	Humus, %	pH of water	Iodine, mg/kg		Bromine, mg/kg	
							total	water-soluble	total	water-soluble
100	Ishim	Ordinary solonetzic	Ad	0–6	7.53	6.39	6.40	<0.001	14.40	3.25
	plain	middle-power	A_1	6–10	6.48	6.52	6.72	0.017	10.60	2.16
	(eastern	middle-humic	A_1	10–20	–	6.72	–	–	6.24	0.90
	part)	middle-loamy	A_1	25–35	7.25	6.31	6.30	0.020	7.00	1.10
		chernozem	AB	40–50	4.63	6.22	5.84	0.040	6.00	0.90
			B	52–62	1.86	6.60	6.36	0.031	2.16	0.40
			BC_k	70–80	1.03	7.16	4.08	0.015	3.12	0.62
			C_k	100–110	–	8.54	–	–	3.95	0.65
			D	140–150	–	7.75	–	–	2.08	–
160	Circum-Ob	Leached	A	0–5	6.65	5.40	6.48	0.037	13.17	3.12
	plateau	middle-power	A_p	5–20	5.05	6.88	6.00	0.046	10.22	1.94
		middle-humic	$A_{p/p}$	35–45	4.05	7.30	5.92	0.040	7.91	1.25
		heavy-loamy	AB	60–70	0.74	7.94	3.04	0.045	5.44	1.00
		chernozem	B	90–100	–	8.85	3.90	0.013	4.15	0.62
			B_k	130–140	–	9.00	4.60	0.010	5.30	0.89
			BC_k	180–190	–	8.86	3.60	0.019	–	–
189	Baraba	Ordinary solonetzic	A	0–20	3.79	6.62	5.68	0.090	11.00	2.52
	plain	shallow weak-humic	B	35–45	0.51	–	4.10	0.073	7.00	1.05
		middle-loamy	B_k	60–70	0.59	–	4.64	0.051	5.15	1.20
		chernozem	BC_k	90–100	0.43	–	2.56	0.036	3.46	0.80
			C_k	150–160	–	8.16	1,52	0.008	4.00	0.95
193	» »	Ordinary solodized	A_p	0–20	3.31	6.97	3.92	0.100	12.45	3.00
		shallow weakly	B_1	45–55	0.54	7.47	3.50	0.500	4.90	1.13
		humic light-loamy	B_{2k}	80–90	0.24	8.34	2.96	0.045	2.10	0.70
		chernozem	BC_k	110–120	0.11	8.41	2.80	0.030	3.20	0.92
			C_k	140–150	–	8.43	2.00	0.024	1.95	–

108	Kulunda plain	Southern solodized shallow weakly humic light-loamy chernozem	A_p	0–20	3.270	6.34	4.00	0.083	9.12	2.18
			B	20–30	1.430	7.86	3.68	0.072	7.22	1.22
			B_k	50–60	0.485	8.52	3.00	0.047	3.63	0.78
			BC_k	–	–	–	–	–	–	–
			C	140–150	0.185	9.55	1.10	0.025	2.05	0.52
162	» »	Southern solodized shallow weakly humic middle-loamy chernozem	A_p	0–20	2.21	6.50	6.0	0.089	7.67	1.46
			AB	30–40	0.67	7.14	5.44	0.063	4.15	0.81
			B_k	50–60	031	8.37	4.24	0.049	2.44	0.63
			BC	100–110	0.10	8.52	1.2	0.015	1.73	0.50
			C	145–155	–	8.77	–	–	–	–
164	» »	Chestnut solodized shallow weakly humic light-loamy soil	A_p	0–20	1.51	6.41	1.92	0.017	3.26	0.90
			B	30–40	0.85	7.30	2.56	0.024	2.17	0.69
			B_k	50–60	0.39	8.31	1.20	0.004	1.70	0.23
			B_k	80–90	0.14	8.56	0.33	<0.001	2.60	0.40
			BC_k	110–120	–	8.86	<0.01	–	2.23	0.47
			C	145–155	–	8.87	<0.01	–	2.80	–
167	» »	Light-chestnut shallow weakly humic light-loamy soil	A_p	0–20	1.07	7.05	1.35	0.013	2.00	0.64
			B_1	40–50	0.63	7.59	1.93	0.018	1.30	0.12
			B_k	70–80	0.23	8.46	0.41	<0.01	2.40	0.75
			BC_k	110–120	0.17	8.56	<0.01	<0.01	2.61	0.37
			C_k	155–165	–	8.58	<0.01	<0.01	2.70	0.43
190	Baraba plain	Chernozem-meadow brackish crusty clayey	A_1	2–6	8.68	6.83	8.52	0.11	4.16	1.00
			B_1	6–15	3.19	8.59	14.32	0.43	13.89	2.63
			B_{2k}	20–30	1.28	9.66	16.0	0.57	33.28	5.13
			B_3	50–60	0.36	9.90	9.20	0.13	30.15	5.00
			BC_k	90–100	–	9.40	2.96	0.05	10.64	1.92
			C	140–150	–	8.95	3.12	0.06	6.31	1.15
207	» »	Chernozem-meadow crusty clayey solonetz	A	0–5	3.90	7.01	2.1	0.02	7.4	3.2
			B_1	5–15	4.40	8.23	7.1	0.07	12.7	3.7
			B_1B_{2k}	20–30	1.97	9.69	10.9	0.24	18.5	5.9
			B_{2k}	50–60	0.29	9.75	13.4	0.61	29.8	7.0
			BC	80–90	0.23	9.47	6.5	0.09	12.3	4.6
			C	120–130	0.22	9.12	4.0	0.03	13.6	4.1

Table 1 (continued)

Cut number	Site of sample collection	Soil	Horizon	Depth, sm	Humus, %	pH of water	Iodine, mg/kg		Bromine, mg/kg	
							total	water-soluble	total	water-soluble
209	Baraba plain	Meadow fine-soddy dark middle-loamy solod	A_1	2–8	6.08	5.7	13.2	0.35	31.5	13.6
			A_2	8–18	1.71	5.9	6.9	0.09	10.2	6.0
			B_1	25–35	0.96	8.6	7.8	0.11	13.4	9.1
			B_2	50–60	0.20	9.3	8.9	0.13	16.8	10.2
			BC_{kg}	90–100	0.19	9.8	7.2	0.11	15.7	8.9
			C_{kg}	140–150	–	9.7	–	–	–	–
211	Kulunda plain	Typical solonchak	A_{sg}	1–5	0.91	10.5	33.2	–	59.4	31.2
			A_{sg}	5–10	0.55	10.3	20.0	–	51.1	24.4
			B_k	10–20	0.61	10.2	–	–	42.6	–
			B_k	20–30	0.73	10.0	11.2	–	44.8	23.9
			BC	70–80	0.15	9.00	9.4	–	39.2	–
			BC	80–90	0.26	8.30	6.9	–	37.4	26.5
208	Baraba plain	Meadow solonchak	A_d	0–5	9.50	7.40	28.8	4.10	54.2	21.3
			A	10–20	6.93	7.90	17.8	1.10	46.4	17.1
			AB	–	–	–	–	–	–	–
			B_{1k}	45–55	0.94	8.30	6.8	0.11	11.3	3.1
			BC_k	75–85	0.53	8.40	6.0	0.10	13.1	3.9
			C	120–130	0.31	8.30	5.6	0.08	12.6	4.5
205	Kulunda plain	Chernozem-meadow brackish fine clayey solonetz	A_1	2–6	4.90	7.30	3.11	0.065	5.77	2.3
			B_{1k}	6–16	4.77	9.40	3.98	0.070	9.15	2.7
			B_{2k}	20–30	2.10	10.0	9.72	0.200	21.4	3.0
			B_{3k}	45–55	0.67	9.70	6.14	0.076	14.1	3.8
			BC_k	110–120	0.11	9.30	4.23	0.050	7.39	2.0
			C	130–170	0.19	9.30	4.00	0.050	–	–

Note. Dash means the absence of analytical data.

amounts of iodine and bromine in them. Maximal humus content here amounts approximately to 3% in the arable horizon and about 0.5 % in the sub one. Besides, these soils are characterized by an acid reaction of the medium throughout the profile and by a wash type of the water regime. That is why the halogens content found is a direct consequence both of the soils' poverty of organic substance that is the principal accumulator of the elements under study, and of the sufficiently high solubility of the majority of bromine and iodine salts, which leads to their active migration under the conditions of the wash water regime. The latter undoubtedly influences also the total content and the amount of water-soluble form of the element. In an acid medium, reactions with participation of iodide and iodate anions are also possible resulting in the formation of free iodine [29], which is subsequently evaporated:

$$5I^- + IO_3^- + 6H^+ = 3I_2 + H_2O \quad (1)$$

$$2I^- + 2NO_2^- + 4H^+ = I_2 + 2NO + 2H_2O \quad (2)$$

In this way, the detected halogen content was quite expected and regular for soddy podzolic soils. The low total halogen content has determined the low amounts of their water-soluble forms.

Gray forest soils of the Vasyugan plain

Here the situation with bromine and iodine accumulation is almost analogous to that in soddy podzolic soils. Although the increase of development of sodding process as compared to the podzol formation seems to have to have determined higher bromine and iodine concentrations, no perceptible accumulation of halogens has taken place. The content of humus – the basic soil indicator of intensity of bromine and iodine accumulation is insignificant (3–4 %). Periodically, the wash type of water regime, which enhances the mobility of humic acids, also tells negatively on their capacity of halogen fixation. The acid reaction of the soil medium in the upper horizons creates favorable conditions for the processes resulting in the formation of free iodine, which is rather undesirable. Besides, the data on the muddy fraction content (11–27 %) also confirm the not high sorption capacity of gray forest soils with respect to halogens. Maximal amounts of bromine and iodine have been found only in the carbonate horizon where their low accumulation due to sorption and occlusion, and some metabolic processes takes place [30]. It was quite expectable to detect, on the background of such total amount of halogens, to find also a low content of water-soluble forms of bromine and iodine. However, one has to note that we compare the data on water-soluble bromine only with the content of the total form.

Chernozems

Soil specimens of leached, usual and southern chernozems were collected in the territory of the Baraba, Kulunda and Ishim plains, and of the Priobskoye plateau. Chernozems' enrichment with organic substance (up to 7–8 %), predominance of humic acids capable of a more active interaction with halogens as compared with fulvic acids in its composition [31] is the priority factor in halogen accumulation processes. In chernozems, the dependence of halogen content on the humus concentration is much tighter than that in soddy podzolic and gray forest soils. The coefficient of correlation with respect to bromine was 0.93–0.96 for leached chernozems, 0.85–0.98 for usual ones and 0.76–0.79 for southern ones; with respect to iodine, it was 0.90–0.94, 0.74–0.88 and 0.70–0.78, respectively. For comparison, $r_{\text{humus-I}}$ was 0.2–0.5 for soddy podzolic soils, and $r_{\text{humus-Br}}$ 0.4–0.5 for gray forest soils. The high sorption capacity of the heavier, mostly clay composition of chernozem soils (physical clay fraction content 40–50 %) with respect to various elements including halogens also contributes to accumulation of the latter. Together with this, under the conditions of reaction of the soil medium which varies from an almost neutral to alkaline one, a most complete assortment of halogen anions is possible [32], which undoubtedly influences their total concentration in the soil. As for the presence of the carbonate horizon capable of sorption and occlusion of various elements and the favorable water regime in chernozems, they only enhance the halogen accumulation. Within the limits of the upper horizon, the water-soluble iodine content corresponds to Yu. G. Pokatilov's criteria. As for the bromine, its content amounts to 20–30 % of the total one.

Chestnut soils

Soil samples were collected in the territory of the Kulunda plain. By the level of iodine and bromine content, they are close to soddy podzolic and gray forest soils. Soil formation on sandy sediments and loess-like blanket light sandy-loams that do not create any barrier to halogen outflow, in combination with such soil properties as the insignificant (up to 1.5 %) humus content, the light granulometric composition (the physical clay content from the upper to the lower horizon varies from 18–22 to 7–9 %), and the wind erosion characteristic of this territory have determined a low content of both total and water-soluble forms of halogens.

Solonchaks

Soil samples were collected in the territory of the lowered Baraba and the northern part of the Kulunda plains. The ridge relief characteristic of these territories was favorable for the formation of salinized soils in its negative forms – interridge hollows. In the solonchaks formed in the lowest places of interridge hollows, very high iodine and bromine concentrations were detected. By means of physicochemical and mechanical migration, haloid compounds with intrasoil and surface outflow are shifted to hollows and concentrated here. Such an active accumulation of halogens with an evident absence of humus witnesses to the fact that their accumulation takes place not only in the humus horizon, but also in the horizons enriched with easily soluble salts; therein, as one can judge by the data obtained, it is even a more considerable one. The high total bromine content has determined also considerable concentrations of the water-soluble form. As to the water-soluble iodine, proceeding from the data obtained, one may hypothesize that it exceeds considerably Yu. G. Pokatilov's criteria.

Solonetzs

The soil samples were taken in the territory of the Baraba and North Kulunda plains. Since the formation of solonetzs, as compared with solonchaks, takes place in more elevated sites, the process of accumulation of halogens here goes less actively. However, it is noteworthy that their iodine and bromine content is nevertheless higher than in zonal soils. The clearly expressed alkaline medium reaction through the whole profile (pH 8–10), enrichment with silt fraction (up to 60 %)and sesquioxides contribute to halogen accumulation. The content of water-soluble halogen forms in solonetzs seems to be determined by the fact that the major part of halogens is fixed by sorption and occlusion mechanisms, which presupposes their desorption by water.

Solods

It is noteworthy that despite the lower salinity, the halogen content in these soils is considerable. One of the main causes of enrichment of solod with halogens is probably the ubiquitous attachment of soils to hollows and the relatively shallow position of ground waters, which create an additional replenishment with various elements, including halogens.

The considerable concentrations of halogens in the solods do not provoke serious concerns, because, due to the natural low fertility, such soils, like solonchaks, are not widely used in agriculture.

The carried out studies permit ascertaining the following things. According to V. V. Kovalsky's and Yu. G. Pokatilov's criteria, the soddy podzolic, gray forest and chestnut soils of the south of West Siberia should be considered as belonging to the group of iodine-poor soils. It is quite possible that the plants grown on these soils will be poor of iodine, too, although we have not found any studies in this field. As far as bromine is concerned, the results obtained witness to the fact that its content in the soil types considered is somewhat higher than that of iodine. It is difficult to judge about the degree of danger of the bromine concentrations studied, because of lack of respective standards.

In this way, in the visible perspective it is necessary to solve the problem of optimal iodine content of soils and to practice a continuous control of element composition of agricultural products grown on them. Besides, it is necessary to carry out detailed studies on bromine supply to the vegetables and establish its optimal content both in various soil types and in plants.

Since the maximal concentrations of halogens in soils used in agriculture have been found in solonetzs, it is necessary to carry out a continuous comprehensive control of iodine and bromine content in this soil, in the vegetable products grown on it and in the composition of fodder consumed by animals.

HALOGENS IN NATURAL WATERS

Studies of iodine and bromine content of natural waters is of practical interest from the point of view of both biogeochemical and hygienic estimation of territories, which will make it possible to estimate the possibility of their use for potable water supply, which is one of the most important tasks of sustainable development. The latter means not only a sufficient amount of potable water, but also its necessary quality. And in the list of elements characterizing the quality, bromine and especially iodine occupy not the last place.

The main forms in which bromine and iodine are found in natural waters include anions G^-, GO^-, GO_3^- and the complex form with inorganic and organic compounds. By the methods of extraction and thin-layer chromatography, the existence of iodine and bromine in subterranean waters in the form associated with organic compounds has been proved [33]. Moreover, in the opinion of some researchers, an important role in the formation of, *e. g.*, iodine organic complexes play by fulvic acids [34].

The influence of pH on the presence of each halogen form can be so considerable that it determines even a change of direction of the chemical process. Thus, for iodine in waters whose pH > 7, dominant are iodide and iodate anions, while in an acid medium it is free iodine, according to the reaction [35]

$$3I_2 + 3H_2O \rightleftarrows HIO_3 + 5HI \quad (3)$$

Besides, characteristic both of iodine and of bromine is a reversible reaction whose equilibrium, in the transition from chlorine to bromine and further on to iodine, is progressively shifted to the left [36]:

$$G_2 + H_2O \rightleftarrows HG + H\Gamma O \quad (4)$$

Therein, the molecular oxygen gradually oxidizes the hydroiode acid under the influence of light already at the usual temperature [36]:

$$O_2 + 4HI = I_2 + 2H_2O \quad (5)$$

so that reaction (5), on the one hand, decreases the water iodine concentration, and on the other hand, the formed iodine goes to the atmosphere, enriches it and returns to natural waters with precipitations. For HBr, reaction (5) goes much slower, which limits the supply of free bromine to the atmosphere.

In an alkaline medium, reaction (6) is also possible [36]

$$G_2 + OH^- \rightleftarrows HOG + G^- \quad (6)$$

However, for acids of HOG type, disproportionation reaction is characteristic [36]:

$$3HOG \rightarrow 2HG + HGO_3 \quad (7)$$

$$5HOG \rightarrow HGO_3 + 2G_2 + 2H_2O \quad (8)$$

Therein, the rates of reactions (5) and (6) rapidly increase from bromine to iodine.

In acid medium, interaction between iodine anions is also possible according to reaction, which results in its loss due to evaporation [29]:

$$5I^- + IO_3^- + 6H^+ = 3I_2 + 3H_2O \quad (9)$$

On the basis of the above-mentioned reactions, one may consider that in alkaline waters iodine is present preferentially in the form of iodide and iodate anions; the presence of insignificant concentrations of free iodine that has not reacted by reaction (6) and of hypoiodide anion not used in reactions (7) and

(8) is also possible. Dominant forms of bromine under alkaline conditions are bromide and hypobromite anions. There may be also free bromine that not entered reaction (6).

In acid medium, prevalent forms of iodine and bromine are iodide and bromide anions and free halogens, mostly iodine.

As to the influence of pH on the forms of complex organic compounds with halogens present in natural waters, it exists and seems to be manifested indirectly through migration capacity of humus. In acid waters, humus migrates very actively, which influences negatively the formation of complex organic compounds with halogens. In neutral and weakly alkaline waters, it migrates very weakly, which certainly contributes to the formation of organic complexes with bromine and iodine. Under strongly alkaline conditions, humus occupies, by the migration intensity, an intermediate position, but in this case the very reaction of the medium ensures not only an active accumulation of halogens, but seems to be able to contribute to the formation of various compounds with halogens, including complex organic ones.

The pH value of the waters studied varies within a range of 7.2 to 8.31 (Table 2), waters of lakes of the Baraba plain being characterized by a higher pH (8.75–10.13), which theoretically contributes to iodine and bromine retaining in the natural waters. However, in reality one has to take into account the processes of adsorption of bromine and iodine by rocks and soils on the way of motion of waters and their volatility that lead to a decrease of the concentration of these halogens. The atmospheric replenishment of waters of the territory under study by halogens is practically ruled out due to its remoteness from seawater areas.

Halogen content of natural water sources is controlled not only by the water medium reaction, but also by the level of water mineralization, which, according to A. I. Perelman's opinion [32], strongly influences the bromine concentration. This is witnessed also by our data on water bromine analysis.

The studies have demonstrated that natural water sources situated in the territory of the south of West Siberia differ in bromine and iodine concentrations (see Table 2). Their maximal concentrations have been found in natural waters of the lowered Baraba plain, which is quite logical. This is a zone of accumulation of easily soluble salts, and here weakly slightly sub saline and brine waters predominate. Therein it is natural that the richest in halogens turn out to be the lakes, which was contributed by their isolation and the absence of outflow, and also the fact that the lakes are water catchments areas for

TABLE 2

Variability of halogen content and pH in natural waters of the south of West Siberia

Geomorphological structure	Waters	pH	Iodine, μg/l	Bromine, mg/l
Baraba	River	7.83–8.30	4.0–20.0	0.41–1.62
	Lacustrine	7.43–10.13	2.7–67.1	0.08–5.70
	Swamp	7.08–8.17	2.0–7.3	Traces – 0.27
	Ground	8.00–8.60	13.6–29.9	0.2–2.96
	Subterranean	7.2–8.57	2.6–25.0	0.23–2.43
Kulunda	Lacustrine	8.10–8.23	16.8–21.0	0.15–1.16
	Ground	6.88–7.55	12.0–14.0	0.4–1.23
	Subterranean	7.44–8.32	8.2–11.3	0.5–1.17
Vasyugan region	River	7.96–8.33	2.0–5.0	0.04–0.10
	Lacustrine	–	0.1–4.2	0.05–0.24
	Swamp	6.90–7.12	<0.1	0.02–0.08
	Ground	6.88	0.9	<0.14
	Subterranean	7.47–7.87	2.0–5.0	0.11–0.18

adjacent elevations and accumulators of salt products of soil formation, which are carried here with the rundown waters. An additional replenishment with salts from lake zones occupied by saline soils is also possible.

The natural waters of the Kulunda plain are mostly sweet and weakly slightly sub saline. Their iodine and bromine content is perceptibly lower as compared to the waters of the Baraba plain, which is determined by the spread of lighter and less saline rocks here.

The waters of the Vasyugan plain, mostly ultrafresh and fresh contain minimal amounts of halogens. The reaction of natural waters is acid and close by neutral (pH 5–6.8), which creates favorable conditions for formation of free iodine that is subsequently evaporate. In swamp waters, the lowest amount of bromine and iodine has been found. The cause thereof, as some researchers think, is the enrichment of these waters with humic acids, and the latter, contributing to iodine sorption in the rocks, do not form stable complexes in water with it [34]. This opinion is in accordance with the data of [37], according to which the iodine forms under the conditions of solution less stable compounds with humic acids than in the solid phase. As for bromine, the low mineralization level of waters hinders its accumulation.

If one compares the results obtained on iodine with the necessary level recommended by endocrinologists (10 μg/l), then one has to recognize the existence of an iodine deficit in the major part of water sources of the south of West Siberia, and this problem has to be solved. Let us also add that there exist still iodine losses due to its volatility associated with water purification and its passage through the water supply networks. Thus, in the Ob – the main source of potable water for the whole region – the iodine content amounts to approximately 20 μg/l, however, in the potable water of Novosibirsk it is only 3.0–3.5 μg/l [38]. It is evident that the constantly low level of iodine in the potable water witnesses to its deficit for the human organism ands must, analogously to fluorination, be compensated for by iodination.

As for the bromine content in natural waters, its concentration lower than the standard ones (0.2 mg/l) is found in some river, swamp and subterranean waters. For example, in potable water of Novosibirsk the bromine content is somewhat lower than the standard and amounts to 0.15–0.18 mg/l, however in the major part of natural water sources it is above 0.2 mg/l. It is obvious that with respect to bromine each case must be considered separately depending on the purpose, for which the water is used.

CONCLUSION

The studies performed have demonstrated that the soil cover of the south of West Siberia is characterized by a considerable variegation in the amount of bromine and iodine determined by differences in their genesis and properties. Therein, the soils contain more bromine and iodine than sol-forming rocks on which they have been formed do. This circumstance is associated with the organic substance of the soil and a higher content of highly dispersed mineral particles in it. The bromine content of the soils considerably exceeds the iodine concentration; at the same time, their distribution pattern in the soil profile is in many aspects equal. The main accumulation of halogens takes place in the humus horizon of zonal soils, in the illuvial and intrazonal soils with a heightened content of easily soluble salts.

In the soils of lowered relief elements, the halogen content is considerably higher than in zonal soils, which are contributed to by their situation in the relief, enrichment with easily soluble salts, sesquioxides and the heavy granulometric composition.

The results obtained on the bromine and iodine in natural waters in the south of West Siberia witness to an iodine deficit of most of them. The hygienic standard for potable water amounts to 10 μg/l. As for the bromine content in water sources of the Baraba and Kulunda plains, it is within the limits of the necessary sanitary norm. The bromine content level in natural waters in the territory of the Vasyugan plain is considerably lower than the necessary criterion.

REFERENCES

1 V. V. Kovalsky, Nauch. Tr. VASKHNIL, Kolos, Moscow, 1972, pp.1–32.
2 V. K. Kashin, Biogeokhimiya, fitofiziologiya i agrokhimiya yoda, Nauka, Leningrad, 1987, 260 p.
3 Yu. G. Pokatilov, Biogeokhimiya biosfery i medikobiologicheskiye problemy, Nauka, Novosibirsk, 1993, 166 p.
4 A. P. Vinogradov, Geokhimiya redkikh i rasseyannykh khimicheskikh elementov v pochvakh, Izd-vo AN SSSR, Moscow, 1957, 234 p.
5 M. A. Mal'gin, Proyavleniye yodnoy nedostatochnosti na Altaye, Gorno-Altaysk, 1988, 55 p.
6 A. P. Larionova, N. S. Spiridonova, *Sel'skokhoz. biologiya*, 4, 3 (1969) 463.
7 N. N. Savitskaya, *Biol. nauki*, 2 (1976) 49.
8 M. Ya. Shkol'nik, Mikroelementy v zhizni rasteniy, Nauka, Leningrad, 1974, pp. 226–229.
9 L. S. Selivanov, *Tr. biogeokhim. lab.*, 7 (1944) 55.
10 B. Ya. Rosen, Geokhimiya broma i yoda, Nedra, Moscow, 1970, 142 p.
11 Ekogeokhimiya Zapadnoy Sibiri, in G. V. Polyakov (Ed.), Izd-vo SO RAN, Novosibirsk, 1996, 248 p.
12 S. V. Semenov, A. A. Monisov, A. I. Rogovets *et al., Melioratsiya i sel. khoz-vo*, 5 (1994) 40.
13 Vrednye khimicheskiye veshchestva, in V. L. Filov *et al.* (Eds.), Khimiya, Leningrad, 1989, pp. 386–396.
14 G. A. Konarbaeva, *Agrokhimiya*, 3 (2001) 85.
15 G. A. Konarbaeva, *Sib. ekol. zhurn.*, 3 (2001) 343.
16 G. A. Konarbaeva, *Geogr. i prirod. resursy*, 1 (2002) 51.
17 V. G. Selyatitskaya, S. Yu. Sukhinina, V. M. Poznyakovskiy *et al., Vopr. pitaniya*, 1 (1996) 27.
18 G. F. Proskuryakova, O. N. Nikitina, *Agrokhimiya*, 7 (1976) 140.
19 G. F. Proskuryakova, *Ibid.*, 8 (1975) 138.
20 A. D. Miller, L. A. Shneider, I. P. Vychuzhanina, L. Ya. Krylova, Metody opredeleniya obshchego soderzhaniya I podvizhnoy fazy yoda i broma v gornykh porodakh i prirodnykh vodakh dlya tseley geokhimicheskikh poiskov, ONTI VITR, Leningrad, 1968, 55 p.
21 V. F. Kamenev, *Khimiya v sel. khoz-ve*, 1 (1965) 26.
22 N. G. Polyanskiy, Analiticheskaya khimiya broma, Nauka, Moscow, 1980, 240 p.
23 E. V. Arinushkina, Rukovodstvo po khimicheskomu analizu pochv, Izd-vo MGU, Moscow, 1979, 486 p.
24 K. B. Yatsimirskiy, Kineticheskiye metody analiza, Khimiya, Moscow, 1967, 199 p.
25 G. S. Fomin, Voda: Entsiklopedicheckiy spravochnik, Protektor, Moscow, 1995, 618 p.
26 Yu. Yu. Lurie, Khimiya, Moscow, 1970, 480 p.
27 J. Sheppard Marsha, J. L. Hawkins, P. A. Smith, *J. Environ Qual.*, 25, 6 (1996) 1261.
28 J. Sheppard Marsha, D. H. Thibault, J. Mcmurry, P. A. Smith, *Water, Air and Soil Pollut.*, 83, 1–2 (1995) 51.
29 У. Дж. Уильямс, Определение анионов, Химия, Москва, 1982, 625 с.
30 G. A. Konarbaeva, *Agrokhimiya*, 12 (2001) 81.
31 R. S. Darer, A. L. Mazurova, A. I. Mun *et al., Izv. AN KazSSR*, 4 (1966) 8.
32 A. I. Perelman, Geokhimiya, Vyssh. shk., Moscow, 1979, 422 p.
33 E. L. Bykova, V. M. Shvets, I. K. Shilov, Rol' vodnorastvorennykh organicheskikh veshchestv v migratsii i kontsentratsii yoda i broma v podzemnykh vodakh. Biologicheskaya rol' mikroelementov i ikh primeneniye v sel'skom khozyaystve i meditsine: Tez. dokl. VI Vsyesoyuz. soveshch., Nauka, Leningrad, 1970, p. 20.
34 S. R. Kraynov, V. M. Shvets, Osnovy geokhimii podzemnykh vod, Nedra, Moscow, 1980, 286 p.
35 H. Remy, Lerbuch der anorganischen Chemie, Bd. 1, Akademische Verlagsgeselschaft Geest & Portig K.-G., Leipzig, 1960.
36 B. V. Nekrasov, Osnovy obshchey khimii, vol. 1, Khimiya, Moscow, 1973, pp. 270–296.
37 F. A. Tikhomirov, S. V. Kasparov, N. I. Ponomareva, *Agrokhimiya*, 3 (1982) 106.
38 G. A. Konarbaeva, K voprosu o kontrole kachestva vody. Tekhnika i tekhnologiya ochistki i kontrolya kachestva vody: Tr. Mezhdunar. nauch.-tekhn. konf., Tomsk, 1999, pp. 194–195.