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Tatiana Perminova

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de doctorat
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Tatiana PERMINOVA

Bromine in the Natural Environments of the Tomsk Region and its Toxicity Assessment

Spécialité :

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ПОЛИТЕХНИЧЕСКИЙ
УНИВЕРСИТЕТ



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THESE

pour l'obtention du grade de

DOCTEUR de l'UNIVERSITE DE TECHNOLOGIE DE TROYES

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DES RESEAUX ET DU DEVELOPPEMENT DURABLE**

présentée et soutenue par

Tatiana PERMINOVA

le 26 octobre 2017

Bromine in the Natural Environments of the Tomsk Region and its Toxicity Assessment

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**BROMINE IN THE NATURAL ENVIRONMENTS OF
THE TOMSK REGION AND ITS TOXICITY
ASSESSMENT**

A dissertation thesis

for the degree of Doctor of University of technology of Troyes

and

Candidate of geological-mineralogical sciences (the Earth sciences)

by Tatiana PERMINOVA

2017

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ABSTRACT

Abstract in English

Bromine in contrast to other, even less common chemical elements, still remains one of the least studied. However, a great number of works show that it can be extremely toxic, exerting a negative impact on important physiological functions of living organisms and participating in the development and formation of certain types of diseases. The objective of this thesis is to establish accumulation and distribution features of bromine in the components of the natural environment of the Tomsk region, and to characterize its human and ecotoxicological impacts according to the USEtox model. This is achieved by combining two approaches: sampling methods and ecological modeling technics. Within the framework of the thesis, the content of bromine in 2709 samples is considered. The reliability of the work is provided by a statistically significant number of samples, analyzed by modern highly sensitive analytical methods (INAA, ICP-MS, X-ray fluorescence analysis, scanning electron microscopy) in accredited laboratories. Also for the first time, characterization factors for bromine have been calculated within the USEtox model. The results obtained could be useful in the future when evaluating the environmental impacts of chemicals and the associated risks for ecosystems and human health as well as for geoecological monitoring of the territory.

Key words:

- Bromine
- Environmental impact analysis
- Environmental geochemistry
- Life cycle analysis
- Risk assessment

Abstract in French

Le brome, contrairement à d'autres éléments chimiques, reste l'un des moins étudiés à ce jour. Cependant, un grand nombre de travaux montrent qu'il peut être extrêmement toxique, exerçant un impact négatif sur les fonctions physiologiques importantes des organismes vivants et participant au développement et à la formation de certains types de maladies. L'objectif de cette thèse est d'établir les caractéristiques d'accumulation et de distribution du brome dans les composantes de l'environnement naturel de la région de Tomsk et de caractériser ses impacts toxicologiques sur la santé humaine et les écosystèmes selon le modèle USEtox. Elle est réalisée en combinant deux approches : les méthodes d'échantillonnage et les techniques de modélisation écologique. Dans le cadre de la thèse, la teneur en brome dans 2709 échantillons est considérée. La fiabilité du travail est garantie par un nombre statistiquement significatif d'échantillons, analysés par des méthodes modernes et hautement sensibles (INAA, ICP-MS, Analyse de fluorescence aux rayons X, Microscopie électronique à balayage) dans des laboratoires accrédités. De plus, pour la première fois, les facteurs de caractérisation d'impact du brome ont été calculés dans le modèle USEtox. Les résultats obtenus pourraient être utiles à l'avenir lors de l'évaluation des impacts environnementaux des produits chimiques et des risques associés pour les écosystèmes et la santé humaine, ainsi que pour le suivi géoécologique d'un territoire.

Mots clés

- Brome
- Environnement - Etudes d'impact
- Géochimie de l'environnement
- Analyse du cycle de vie
- Evaluation de risque

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INTRODUCTION

Relevancy

Bromine in contrast to other, even less common chemical elements, still remains one of the least studied. Work on the issues of its accumulation and migration in the environment has been carried out by a number of researchers and has shown the ambiguous behavior and high indicator properties of the element. Most of the publications available are devoted specifically to the consideration of natural features of the behavior of bromine in the environment. However, greater attention should be paid to the study of its techno geochemistry, due to its wide use in numerous spheres of human activity: agriculture, medicine, chemical, food, pharmaceutical industries, etc.

Bromine is one of the most important participants in the formation of the food chain: atmosphere - soil - natural water - plants - animals - man. A "symbiosis" of natural and anthropogenic sources of the element, determining the complex and multifactorial nature of its entry into the environment, undoubtedly influences the features of accumulation and distribution of the halogen, both in each individual link of the above described food chain, and in its totality.

The Tomsk region is of particular interest from the point of view of studying of bromine due to the presence of a large number of potential natural (oil and gas fields, peat, coal, groundwater, including iodine-bromine sources, etc.) and anthropogenic sources of the element in this territory. The latter are concentrated, mainly, in the Tomsky district of the region, namely in the Northern Industrial Zone. The entry of the element into the environment of the region may also be related to vehicle emissions and air transport since the "Bogashevo" airport is the main operating international airport of federal significance within the Tomsk region.

At the same time, the important question is the choice of the best way to evaluate environmental status, allowing the characterization of the toxic effects of chemicals for ecosystems and for human health. This is due to the fact that bromine can be extremely

toxic, exerting a negative impact on important physiological functions of living organisms and participating in the development and formation of certain types of diseases. Bromine is one of the elements, which most often leads to an increased risk to human health, at least 11 different pathologies are associated with the element.

The availability of a significant number of modern environmental impact assessment ways makes it possible to carry out a comprehensive analysis using various methods, approaches, concepts and models that allow prediction of adverse effects on living organisms, including human health. From the point of view of studying the toxicity of chemical elements, methods of ecological modeling are becoming more widespread and offer a number of advantages. Therefore, they are of great interest in geocological studies of a territory.

Among existing ecological models for assessing toxic effects on ecosystems and human health, the USEtox model deserves particular attention. It was developed by the Society for Environmental Toxicology and Chemistry (SETAC) in 2010 and recommended for use by the world scientific community: UNEP, EPA, the European Commission and others. One of the advantages of the model is the consideration of the multifactor effect of chemical elements: their intake by inhalation and oral routes are taken into account. Another important advantage, showing the uniqueness of the model and its relevance in the context of environmental studies, is the consideration of specific landscape-geographical and climatic features of a territory.

To calculate the toxic effects of chemical elements on ecosystems and human health, a knowledge of their characterization factors (CFs) and masses in an environmental media is necessary. If the data on the quantitative content of the element is the result of analytical studies, the calculation of the CFs is carried out according to the methodology proposed in the model. CFs are based on the physicochemical properties of the elements, the features of their behavior in the environment (for example, their degradation rates in air), and on the data of toxicological studies, obtained in experiments on experimental animals and extrapolated to humans. Nowadays, the USEtox model database includes information on CFs for more than

3000 organic compounds and 25 inorganic elements (As, Cr, Co, etc.). However, there is no CF for bromine, which also indicates the relevance of this study.

Study objective

The objective is to establish accumulation and distribution features of bromine in the components of the natural environment of the Tomsk region, and to characterize its human and ecotoxicological impacts according to the USEtox model.

Principle tasks

- To perform a literature review on geoecological aspects of the accumulation and distribution of bromine in natural and technogenic landscapes;
- To determine the quantitative content of the element in the various components of the natural environment in the territory of the Tomsk region and compare the data with other regions of Russia and abroad, as well as literature sources.
- To analyze the spatio – temporal distribution of bromine over the study area with the designation of local areas, characterized by higher contents of the element, caused by natural and technogenic factors;
- To conduct a ranking of the territory of the Tomsk region in accordance with the minimum – maximum concentration of element in environment components;
- To set indicators of the relations of bromine with chemical elements in the vicinity of industrial enterprises;
- To develop human toxicity and freshwater ecotoxicity characterization factors for bromine, by using the USEtox model;
- To characterize human and ecotoxicological impacts of bromine on the example of soils of the Tomsk region, taking into account its landscape-geographical characteristics, and to make an analysis of the results obtained with the data on diseases of the population of the Tomsk region;
- To conduct the ranking of the region's territory according to the degree of risk to ecosystems and human health.

Principal propositions to be confirmed in this thesis

1. Within the framework of bromine circulation in natural and anthropogenic systems, it is established that the specificity of the Tomsk region is the substantial accumulation and extremely heterogeneous distribution of the element in terrestrial plants, animals and human bodies. As for abiotic components, significantly higher bromine concentrations are observed in the soils of the Bakcharsky and the Kozhevnikovsky districts relative to the average in the region, although other environmental media in these territories do not show such abnormal levels.
2. The specificity of bromine accumulation in the environmental media depends on the nature and complexity of the natural and anthropogenic impact, and is manifested in the associative relationships of the element, the unevenness of its concentration over time, and the decrease in the content with the distance from the technogenic zone.
3. Based on the results obtained on the characterization factors for bromine, it is established that the contribution of the element to the toxicity indicator is higher for ecosystems than for human health. The ranking of the administrative districts of the Tomsk region in terms of the toxic effect of bromine, taking into account its landscape and geographical characteristics, shows that the highest risk for the health of the inhabitants due to the content of bromine in soils is observed for the Bakcharsky district, whereas for the ecosystems for the Tomsky district. However, bromine makes a minimal contribution to the general toxicity score.

Materials and research methods

The dissertation is based on the results of studies conducted personally by the author, as well as jointly with the staff of the Department of Geoecology and Geochemistry of the Institute of Natural Resources of Tomsk Polytechnic University. The work also includes material provided by colleagues from the universities and institutes of Tomsk (Tomsk State University, Siberian State Medical University,

Scientific Research Institute of Pharmacology); Pavlodar (Pavlodar Pedagogical Institute); Novorossiysk (Institute of Biochemical Geochemistry, Southern Federal University); Ulan-Ude (Buryat State University), and others too numerous to mention.

Within the framework of the work, the content of bromine in 2709 samples is considered. Among them 408 soil samples, 19 samples of coals, 36 samples of bottom sediments, 8 drinking water samples, 317 samples of salt deposits (scale of drinking water) and 34 food samples, as well as 1887 samples of living matter, including human organs and tissues, some vegetation and mammal species. The main sampling area is the Tomsk region, data from other regions of Russia and abroad were considered for comparative analysis.

For the quantitative determination of bromine in the environmental media, the following methods were used: instrumental neutron activation analysis (INAA), inductively coupled plasma mass spectrometry (ICP-MS), and X-ray fluorescence analysis (XRF). Several samples of biomaterials were studied using scanning electron microscopy (SEM). All selected materials were analyzed in accredited laboratories according to certified methodologies, by using standard reference samples. Reliability of analyzes was confirmed by control determinations on different media, internal control was performed.

Reliability of proposition

is provided by a statistically significant number of samples, analyzed by modern highly sensitive analytical methods (INAA, ICP-MS, X-ray fluorescence analysis, scanning electron microscopy) in accredited laboratories, and by the depth of consideration of material, using modern statistical processing methods and literature on the research topic.

Scientific novelty

For the first time a comprehensive analysis of the peculiarities of the accumulation of bromine in a significant number of environmental components has been done. The

features of the space-time distribution of the element in the territory of the Tomsk region within its various natural-anthropogenic conditions are considered.

Also for the first time, characterization factors for bromine have been calculated within the USEtox model. Human and ecotoxicological impacts of bromine were established on the basis of the calculated CFs and the results of Br concentrations in the soils, taking into account the landscape and geographical features of the Tomsk region. Finally, a risk ranking of the territory of the Tomsk region on the appropriate scales for ecosystems and human health was carried out.

Practical significance

Based on the results of the study, geochemical maps of bromine distribution in various environmental media were created. The district differentiation of the Tomsk region, that may be useful for geoecological monitoring of the territory, was carried out according to the levels of bromine concentration in the environment.

Data on the CFs for bromine, previously not accessible in the USEtox model, were obtained. In the future, the results for the Tomsk region as a separate landscape geographical area, obtained within the model, can be used for conducting geoecological studies in order to study the toxicity of chemical elements and the associated risks for ecosystems and human health.

The results of the work were used to conduct lectures and practical exercises in the course "Introduction to Environmental Science and Engineering" at the UTT (France) for the training of engineers. They could also be used in the courses "Ecology", "Geochemistry of living matter" and "Medical Geology" for the preparation of bachelors and masters in the specialties "Ecology and environmental management" at the Department of Geoecology and Geochemistry of the Institute of Natural Resources of Tomsk Polytechnic University.

Work approbation

The main results of the dissertation thesis were discussed at Russian and International Symposiums and Conferences:

- the International Scientific Symposium of Students and Young Scientists of academician M.A. Usov "Problems of geology and mineral resources development" (Tomsk, 2011-2013, 2015-2017);
- "Ecology of Southern Siberia and adjacent territories" (Abakan, 2012);
- International scientific-practical conference "Theoretical and applied problems of science and education (Tambov, 2015);
- II Russian Scientific Conference "Malyshev Readings" (Stary Oskol, 2015);
- IX International Biogeochemical School "Biogeochemistry of Technogenesis and Contemporary Problems of Geochemical Ecology" (Barnaul, 2015);
- International Conference "Ecodesign" (Tokyo, Japan, 2015);
- International Conference "Radioactivity and Radioactive Elements in the environment" (Tomsk, 2016);
- International Conference "The International Society for Ecological Modeling Global Conference 2016" (Towson, USA, 2016).

In addition, the results of the thesis were reported at scientific seminars at the GEGH department of TPU (Tomsk, Russia), in CREIDD at the UTT (Troyes, France), as well as at the Department of hydrology and geochemistry of the University of Strasbourg (Strasbourg, France).

Within the PhD thesis, the author also participated in the scientific summer school "Toxicology and Environmental Health" (Utrecht, the Netherlands, 2015), and "USEtox summer school" (Copenhagen, Denmark, 2016).

Publications

The main content and scientific results of the thesis are published in 20 articles and abstracts, including 2 articles in peer-reviewed journals included in the Higher

Attestation Commission list and 1 article in English in a journal with IF 2.9, indexed in the Scopus database.

Thesis structure and volume

The thesis consists of an introduction, 8 chapters, a conclusion, a bibliography, and an appendix, set out on 263 pages of typewritten text. It includes 77 figures and 33 tables. The bibliography contains 354 sources.

In the **introduction**, the relevance of the study, the objective and tasks, the main results, the scientific novelty and practical significance, as well as the author's personal contribution and approbation of the work are presented.

In the **first chapter**, ecological and geochemical features of bromine, its physico-chemical properties, effects on living organisms, as well as hygienic standards are considered.

The **second chapter** presents an extended review of the literature on bromine, the levels of its accumulation in environmental media and the main areas of application of the element and its compounds.

The **third chapter** is devoted to the analysis of existing methods of environmental evaluation.

The **fourth chapter** contains information on the research methods, sampling, subsequent preparation, mathematical data processing and the methodology of the USEtox model.

The **fifth chapter** considers a brief natural climatic and geocological characteristics of the territory of Tomsk region.

The **sixth chapter** is devoted to the peculiarities of accumulation and distribution of bromine in the biotic and abiotic components of the environmental media of Tomsk region. The analysis of the levels of bromine accumulation in the components of the environment of Tomsk region in comparison with other territories of the Russian Federation and abroad is carried out.

The **seventh chapter** presents the features of the distribution of bromine in conditions of technogenesis of the Tomsky district of the region. An analysis of the

change in the contents of the element over the years has been carried out. The geochemical specificity of the components of the environment in the areas near oil refineries has been studied, and indicator ratios of bromine with other chemical elements are considered.

The **eighth chapter** reviews the toxic effects of bromine on ecosystems and human health, using the USEtox environmental model. The analysis of the interrelations between the toxicity of bromine in soils and the level of morbidity of the population of Tomsk region was carried out.

In **conclusion**, the main results and conclusions of the thesis work are discussed.

Personal author's contribution

consists in the selection and preparation of 266 samples. Sampling was carried out on the territory of the Tomsk region (soils, drinking water, scale of drinking water, children's hair, human blood, microorganisms of mineral springs, vegetation, food), in the Grand Est region in France (soil, drinking water, poplar leaves), and in the Baikal region (microorganisms of mineral springs). In addition, the author also synthesized additional material, including 2433 samples.

The author personally carried out statistical processing of all data, gave the interpretation of the results obtained, and formulated the states proposed. The author calculated the CFs for bromine as well as introducing the Tomsk region into the USEtox model as a separate landscape-geographical zone in the course of joint work with P. Fantke, O. Jolliet.

**CHAPTER 1. ECOLOGICAL AND GEOCHEMICAL
PECULIARITIES OF BROMINE**

1.1 General characteristic of the element

In the periodic system of chemical elements of D. I. Mendeleev, **bromine** – **Br** (*lat. Bromum*) has an atomic number of 35 and an atomic mass of 79,904. It belongs to the group of halogens, which in addition to this element, includes also fluorine, chlorine, iodine, radioactive astatine and tennessine (Figure 1.1). Under normal conditions, it is a heavy (density – 3,102 g/cm³ at 25°C) red-brown liquid with a sharp disagreeable odor. Bromine is one of the two simple elements (along with mercury), and the only nonmetal, that is liquid at room temperature.

Period	Group																	
	I	II	III	IV	V	VI	VII	VIII	IX	X	XI	XII	XIII	XIV	XV	XVI	XVII	XVIII
1	¹ H																	² He
2	³ Li	⁴ Be											⁵ B	⁶ C	⁷ N	⁸ O	⁹ F	¹⁰ Ne
3	¹¹ Na	¹² Mg											¹³ Al	¹⁴ Si	¹⁵ P	¹⁶ S	¹⁷ Cl	¹⁸ Ar
4	¹⁹ K	²⁰ Ca	²¹ Sc	²² Ti	²³ V	²⁴ Cr	²⁵ Mn	²⁶ Fe	²⁷ Co	²⁸ Ni	²⁹ Cu	³⁰ Zn	³¹ Ga	³² Ge	³³ As	³⁴ Se	³⁵ Br	³⁶ Kr
5	³⁷ Rb	³⁸ Sr	³⁹ Y	⁴⁰ Zr	⁴¹ Nb	⁴² Mo	⁴³ Tc	⁴⁴ Ru	⁴⁵ Rh	⁴⁶ Pd	⁴⁷ Ag	⁴⁸ Cd	⁴⁹ In	⁵⁰ Sn	⁵¹ Sb	⁵² Te	⁵³ I	⁵⁴ Xe
6	⁵⁵ Cs	⁵⁶ Ba	La-Lu	⁷² Hf	⁷³ Ta	⁷⁴ W	⁷⁵ Re	⁷⁶ Os	⁷⁷ Ir	⁷⁸ Pt	⁷⁹ Au	⁸⁰ Hg	⁸¹ Tl	⁸² Pb	⁸³ Bi	⁸⁴ Po	⁸⁵ At	⁸⁶ Rn
7	⁸⁷ Fr	⁸⁸ Ra	Ac-Lr	¹⁰⁴ Rf	¹⁰⁵ Db	¹⁰⁶ Sg	¹⁰⁷ Bh	¹⁰⁸ Hs	¹⁰⁹ Mt	¹¹⁰ Ds	¹¹¹ Rg	¹¹² Cn	¹¹³ Uut	¹¹⁴ Fl	¹¹⁵ Uup	¹¹⁶ Lv	¹¹⁷ Ts	¹¹⁸ Uuo

Figure 1.1 – Bromine in the periodic system of chemical elements of D. I. Mendeleev. The gray color denotes the elements of the halogen group, in red the chemical elements – "neighbors" of bromine are shown. The figure was created by the author, using the table of D. I. Mendeleev and data of A.I. Perel'man, 1979.

At the temperature of -7.25 ° C it solidifies, forming brown crystals of acicular shape, when boiling (boiling point + 59.5 ° C), it turns from liquid into brown vapors (*Chemical Encyclopedia, 1988*). In the free state, the element has a diatomic structure of Br₂ (Br₄ molecules are found in vapors) due to its high volatility and low evaporation enthalpy (*Greenwood, 2008*).

Bromine has two natural isotopes: ⁷⁹Br and ⁸¹Br, the percentages are almost the same: 50.57% and 49.43%, respectively (*Polyansky, 1980*). However, there are

numerous radioactive isotopes of the element, obtained by artificial means, with mass numbers from 68 to 97. Almost all of them are short-lived, with the exception of ^{77}Br and ^{82}Br , whose half-lives are 57 h and 35.3 h respectively (*Audi, 2003; Eggenkamp, 2014*). This halogen is also present in chains of radioactive decay, with the formation of krypton and other elements in the following way: $\text{Br}^{82}-\text{Kr}^{82}-\text{Rb}^{82}-\text{Sr}^{82}-\text{Y}^{82}-\text{Zr}^{82}$ (*Gusev, 1978*). Similar chains are observed for almost all radioactive isotopes of bromine.

In the outer electron level of a bromine atom there are seven electrons ($3d^{10}4s^2 4p^5$), it lacks only one electron to achieve a stable configuration layer, that it can easily attach. Due to the presence of an unfilled p sublayer, Br can have a variable valence in compounds: -1 (bromides, for example, KBr), +1 (hypobromite, NaBrO), +3 (bromite, NaBrO₂), +5 (bromate, KBrO₃), +7 (perbromates, NaBrO₄). Bromine, like other halogens, is characterized by high chemical activity because of the tendency of its atoms to become negative monovalent ions (*Remi, 1963*). The element's reactivity is intermediate between chlorine and iodine: it is more reactive than iodine, but less than chlorine.

Under normal conditions, bromine is moderately soluble in water: 3.5g/100 g of water at 20°C (*Bikkulova, 1999*) and, to a limited extent, is subjected to dismutation ("bromine water"). The solubility of the element increases in the presence of bromides and chlorides and decreases in the presence of sulfates (*Lidin, 2000*). In the aqueous environment, bromine is able to oxidize nitrites to nitrates, sulfur and sulfites to sulfuric acid, ammonia to nitrogen, and iodides to free iodine. Since bromine is a strong oxidant, it reacts with almost all non-metals and many metals. Under normal conditions, the element does not react directly with O₂, N, and C. Reaction with hydrogen occurs at elevated temperatures with the formation of hydrogen bromide. In aqueous solution of bromides, Br is oxidized by Cl₂, KMnO₄, K₂Cr₂O₇, H₂O₂ to Br₂ (*Chemical Encyclopedia, 1988*).

With other elements of the halogen group, bromine forms unstable, highly reactive compounds: BrF₃, BrF₅, BrCl and BrI. The desire to charge negatively

determines the peculiarity of halogens, which consists of replacing each other from the compounds. As a consequence, elemental fluorine displaces Cl, Br and I from their compounds with metals, chlorine displaces Br and I, and bromine only iodine. However, from oxygenated acids and their salts, in which the halogens are positively charged, the order is reversed: iodine displaces chlorine and bromine, and bromine displaces chlorine (*Remi, 1963*).

Bromine is a typical trace element, which explains the "universality" of its distribution and presence in all environmental compartments. Due to its high chemical activity, the element is mobile in any geochemical environment, easily migrates in the form of soluble compounds, rarely forming a solid mineral form (*Perel'man, 1989*). According to the main geochemical properties Br corresponds to the atmo-, bio – and hydrophilic elements, and, by the main mineral-geochemical features, to lithophilic ones (*Ivanov, 1996*). The main geochemical barriers are the organogenic and evaporation (*Alekseenko, 2000; Chertko, 2008*).

1.2 Influence on living organisms

Despite the fact that bromine is an essential element, in excessive amounts it can have adverse effects on all living organisms. There is considerable data indicating the toxic effects of bromine, and its specific role in the formation and development of several types of diseases.

1.2.1 Toxicity

Bromine can be extremely toxic to plants, because it can replace the chlorine necessary for them, and affect a change in the permeability of cell membranes (*Kabata-Pendias, 2011; Nazer et al., 1982*). The toxicity of the element for plants is manifested in chlorosis, i.e. in a violation of the formation of chlorophyll and a decrease of the activity of photosynthesis, with subsequent necrosis of the leaves. The use of citrus fruits is widely known as an indicator of the toxicity of bromine: a decrease in their growth rate correlates positively with the content of water-soluble bromine in soils. Bromine concentrations of 20 mg/kg in the surface layer of the soil are considered to be limiting in relation to phytotoxicity (*Kabata-Pendias, 1989*).

A study of the effect of bromine on hydrobionts showed that exposure to doses of 400 mg/l for 30 min to 1 h 10 min, or 100 mg/l over 1-3 h, or 20 mg/l over a period of 15 to 96 h, were fatal to fish (*Metelev, 1971*). Crucian carps die when the concentration of bromine is 20 mg/l, for chlorella this concentration is 0.18 mg/l, and for annelid worms is 0,14 mg/l (*Glushko, 1979*).

A number of studies on experimental animals have also investigated toxicity of bromine. Determination of acute bromine toxicity showed that, when injected into the stomach, the average LD50 dose is: for mice – 3100-7000 mg/kg (*Groff, 1955; Voss, 1961; WHO, 1988; IUCLID., 2000*); for rats 2600-3500 mg/kg (*Smith, 1925; WHO, 1988; IUCLID., 2000*); for rabbits – 2500-4600 mg/kg, and for guinea pigs – 5500 mg/kg (*WHO, 1988; IUCLID., 2000*). Median lethal concentration LC50 is equal to 2900 mg/m³ for mice and 2700 mg/m³ for rats. When the concentration is 1200-200 mg/m³, bromine vapor is lethal for cats, rabbits and guinea pigs. Regarding the influence on cardiovascular and endocrine systems, the threshold concentration of bromine is 50 mg/m³, and the effect on spermatogenesis is 100 mg/m³ (*Ivanov, 1996*).

The results of a short-term toxicity show that when a 99.5% solution of sodium bromide at 19200 mg/kg is absorbed for 4 weeks, rats lose motor coordination of the hind limbs (*van Logten, 1973*). However, when the same level of sodium bromide is absorbed with a low chloride diet (a decrease in the chlorine content from 11 g/kg to 3 g/kg), a lethal effect is observed within 12 days (*Kroes et al., 1974*).

The results obtained in chronic experiments indicate important clinical and physical symptoms of bromide poisoning: weight loss, endocrine, cardiovascular and nervous system dysfunction of rats, and disturbances in the respiratory system of rabbits at a concentration of 12.4 mg/m³. Introducing bromine into rats' stomachs over a three-month period caused changes in carbohydrate and protein metabolism, increased blood sugar and decreased the content of ascorbic acid in the adrenal glands. Almost half of the experimental animals showed focal alopecia. The introduction of brominated vegetable oil to rat feed for 1-6 months led to liver degeneration and degenerative necrotic changes in the myocardium (*Harmful chemicals, 1988*).

In addition to direct toxic effects, bromine is also characterized by long-term effects, affecting fundamental functions of living organisms, primarily reproductive (*Arbuzova et al., 2013*). According to the experiments of *Van Leeuwen (1983)*, complete infertility was observed in a group of rats fed with 19.200 mg/kg of sodium bromide. In the group receiving a 4800 mg/kg dose, the fertility and viability of the offspring decreased. In groups with a dose of sodium bromide 0.75 mg/kg and 300 mg/kg there were no changes. In addition, the work of *Canton (1983)* shows a decrease of the newborn juvenile fish when exposed to bromine for 124 days at a dose of 7.8-78 mg/l. This fact is of particular importance as it indicates that bromine is an environmentally toxic element, since it creates a threat not only for individual organisms, but for entire populations and generations.

For humans, bromine is toxic no matter which way it enters the body. Particular attention should be paid to the inhalation path of the element in view of the fact that bromine is rapidly absorbed by the lungs. *Mogosh (1984)* notes that the effects of airborne bromine can be as follows: suffocation, noted at concentrations of 11-23 mg/m³; severe toxic effects - at 30-60 mg/m³ and death - at 220 mg/m³. Workers, engaged in the production of elemental bromine and its compounds, suffer from carbohydrate metabolism and kidney function disorders, and a decrease in the activity of the thyroid gland (*Shapovalov, 1974; Shapovalov, 1974a*).

1.2.2 Bromine and human health

Bromine, along with nickel, vanadium, aluminum, arsenic and silicon, is one of the elements that most often leads to an increased risk to human health (*Valdés, 2012*). As a trace element, it can play an important role in the appearance and development of various diseases. According to *Avtsyn (1991)*, there are 11 different pathologies associated with bromine, which characterizes the element as having high pathological properties (P = 4).

Lin et al. (1985), as well as *Sarmani et al. (1990)* confirm that bromine can be important in the formation of kidney stones. Elevated element concentrations were detected in the cardiac tissues of patients with uremia (*Pehrsson et al., 1983*), dilated

cardiomyopathy (*Bumbalova et al., 1991*), sickle cell anemia and malignant breast tissue (*Ehmann et al., 1996*). High concentrations of bromine are observed in the brain (75% of the cerebral cortex), hair and nails of patients with Alzheimer's disease (*Ehmann et al., 1996*). Correlation analysis revealed a positive association of liver cancer with bromine content in water (*Litch, 2005*), skin diseases with bromine content in the scale of drinking water, and negative - with diseases of the digestive system and the circulatory system (*Arynova, 2016*).

In addition, numerous data, cited by both Russian and foreign researchers, demonstrate a possible relationship between thyroid pathologies and bromine. According to *Vobecky et al. (1996)*, the increasing iodine deficiency, observed in many countries today, is associated with a high accumulation of bromine in the environment. Br is one of the strongest competitors of iodine for active enzyme centers (*Verkhovskaya, 1962, Krivobok, 1972, Avtsyn, 1991*), it is able to prevent its absorption (*Pavelka, 2001*), and it also reduces iodine quantity in the thyroid gland, skin and breast milk (*Pavelka, 2002*). It has been noted that high levels of bromine are observed in people with thyrotoxicosis (*Verkhovskaya, 1962*). In addition, the data of *Denisova et al. (2011)* indicates a link between bromine and incidence of diffuse nontoxic goiter. According to *Turetskaya (1963)*, the bromine content in the pathologically altered thyroid gland is more than 10 times higher than in a normal thyroid gland.

In view of the foregoing, it is highly important to consider the quantitative content of bromine in the human body under various pathological conditions (Table 1.1).

Table 1.1 – Content of bromine in the body of people, suffering from different diseases

Disease	Research object	Content, mg/kg ¹	Research details	References
Obesity	Hair	17,0 ± 5,0	–	<i>Zhuk, et al., 1995</i>
		17,0 ± 3,2	–	
Diabetes mellitus	Blood	3,6 ± 0,02 mg/ml	–	<i>Ward et al., 1984</i>
Cataract	Crystalline lens	1,0 ± 0,5 μs/s	Residents of the Czech Republic (50-80 years)	<i>Stverak et al., 1988</i>

¹ Unless otherwise indicated

Disease		Research object		Content, mg/kg	Research details	References
Malignant formations	Breast	Blood		23,2 ± 3,6	Residents of India	<i>Sarita, et al., 2012</i>
		Hair		6,1 ± 0,7	Residents of Uzbekistan	<i>Zhuk, et al., 1995</i>
	Rectum			23,0 ± 3,8	–	
	Stomach			24,0 ± 4,6	–	
	Brain	Brain	Core	0,219 ± 0,147 mg/g	–	<i>Zheng et al., 1992</i>
			Mitochondria	< 0,094 mg/g	–	
			Myelin	0,044 mg/g	–	
			Synaptosome	< 0,030 mg/g	–	
	Lungs	Bone		15,8	–	
				10,0	–	
Urolithiasis disease	Stones in the kidneys	Uric	34,4 ± 5,8	Inhabitants of Kuala Lumpur (Malaysia)	<i>Sarmani et al., 1989</i>	
		Calcium oxalate	11,4 ± 8,4			
		Xanthine	6,4 ± 0,7			
Congenital myocardosis	Hair		4,3 ± 0,9	Children (Uzbekistan)	<i>Zhuk, et al., 1995</i>	
Cerebral leptomeningitis			28,0 ± 6,0	Inhabitants of Uzbekistan		
Thrombosis of the vessels of the brain	Bone		19,3	–	<i>Hyvonen-Dabek et al., 1981</i>	
Fibrotic alveolitis			5,5	–		
High blood pressure			20,3	–		
Aortic and mitral insufficiency			8,2	–		
Subarachnoid haemorrhage			11,2	–		

As it can be seen from the table, there are changes in bromine levels in the human body with various pathologies. The type of treatment and medications taken also play an important role in the fluctuations of the element in the body. Thus, the content of bromine in the blood and urine of patients who underwent three-week treatment in the balneological centre in Australia increased significantly (from 2.31 mg/l at the beginning of treatment to 9.53 mg/l at the end) and (from 1.40 to 3.88 mg/g) respectively (*Buchberger et al., 1989*). For the case of diabetes: $3,57 \pm 0,024$ mg/ml of

bromine was found in the serum of patients with diabetes who received insulin treatment; compared with $3,26 \pm 0,47$ mg/ml for those who did not receive any treatment. The level of bromine in the serum of people not suffering from diabetes was $3,66 \pm 0,20$ mg/ml (*Ward et al., 1984*).

Studies of *Metairon et al. (2009)* show that in the blood of patients with chronic kidney disease, the content of bromine varies depending on the type and duration of treatment. The authors studied the distribution of bromine in the blood of sick men and women from 25 to 66 years old, living in Brazil. Patients were divided into 4 groups, with 6 patients in each, depending on the type and duration of treatment. The ^{80}Br content in the first group of patients for whom conservative treatment was applied (only medical and food control for 17 months) was 31 ± 4 mg/l; in the second (undergoing peritoneal dialysis for two years) - 25 ± 10 mg/l; in the third (hemodialysis for 2 years) - 20 ± 9 mg/l; in the fourth group (hemodialysis for 5-11 years), the content of the element was significantly lower - 6 ± 7 mg/l. Thus, it was found that bromine in the blood is removed by hemodialysis or peritoneal dialysis, and that the level of bromine in the blood of patients on chronic hemodialysis is below normal (*Tomza et al., 1984*).

In drugs, the following bromine content (mg/g) was found: amoxicillin – $0,56 \pm 0,04$; atenol – $1,98 \pm 0,12$; clavulanic acid – $3,41 \pm 0,16$; clonazepam – $1,99 \pm 0,16$; haloperidol – $7,75 \pm 0,62$; imipramine – $4,37 \pm 0,26$; nimesulide $< 0,02$; diltiazem – $6,18 \pm 0,28$; propranolol – $4,5 \pm 0,37$; diclofenac – $13,4 \pm 1,0$ (*Muller et al., 2012*). In 5 grades of aspirin in Egypt, 0,08-0,4 mg/kg bromine was found (*Iskander et al., 1986*), and in American brands 0-9 mg/kg (*Hichwa et al., 1981*).

Due to widespread use of bromine for medical purposes, there is a serious problem associated with its iatrogenic pathologies (*Avtsyn, 1991*). Increased consumption of bromine and overdose during treatment can cause depression of the nervous system, drowsiness, ataxia, decreased pain sensitivity, hearing, vision and memory loss, psychotic disorders, accompanied by visual, auditory and other hallucinations. Chronic poisoning with bromine and its compounds (bromism) is manifested by catarrhal rhinitis, bronchitis, and skin lesions (bromoderm).

1.3 Hygienic standards in Russia

Despite the widespread use of bromine today, the potential danger caused by anthropogenic entry of the element into the environment, as well as its negative impact on living organisms, today there are not only significant gaps in the establishment of hygienic standards for the element, but also their complete absence.

In fact, in Russia, bromine is standardized in atmospheric air and in water. In atmospheric air, the following standards apply for this element: the maximum permissible concentration (MPC) in the workplace is 0.5 mg/m³ (*GN 2.2.5.1313-03*), MPC in public areas – 0.04 mg/m³ (*GN 2.1.6.1338-03*). According to these standards, bromine presents a class II danger, i.e. is highly dangerous. The established hygienic standards for bromine in water include: MPC in aquatic objects of economic-drinking and cultural-household water use – 0,2 mg/l according to sanitary-toxicological index (*GN 2.1.5.1315-03*), MPC for drinking water (*SanPiN 2.1.4.1116-02*) and also MPC for waters of fishery reservoirs – 1,35 mg/l (*The list*, 1995).

However, there is a complete absence of any standard for bromine in soils. There are also no standards for this halogen in food. Sanitary-epidemiological rules and regulations indicate several food additives containing bromine that are banned for use in food production, such as potassium and calcium bromates, used as flour and bread improvers, and bromelain, used as a stabilizer, an accelerator of ripening of meat and fish, and a taste and aroma enhancer (*SanPin 2.3.2.1078-01*).

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**CHAPTER 2. GEOECOLOGICAL ASPECTS OF
ACCUMULATION AND DISTRIBUTION OF BROMINE IN
NATURAL AND TECHNOGENIC SYSTEMS**

For a full, comprehensive analysis of the patterns of accumulation and distribution of bromine in the environment, it is extremely important, in our opinion, to study the element within the functioning of the biosphere, in the unity of its inextricably interconnected biotic and abiotic components. *V. I. Vernadsky (1922), V. I. Vernadsky (1994)* noted that it is impossible to consider the components of the biosphere in isolation from each other. The biosphere includes the atmosphere, hydrosphere, living matter and the upper part of the earth's crust, with a very uncertain position of the border (*Yaroshevsky, 2004*). All components are interconnected by flows of matter and energy and should not be viewed as isolated links, but as an interconnected whole. This approach allows us not only to study in quantitative terms the content of the element in individual components of the environment, but also to consider the successive links of the biogeochemical food chain in their entirety. In addition, it allows the relationship between the geochemical factors of the environment and living organisms to be traced.

Based on the literature data, we considered the balance of bromine distribution in biosphere reservoirs within the framework of the element's cycle in the nature (Figure 2.1).

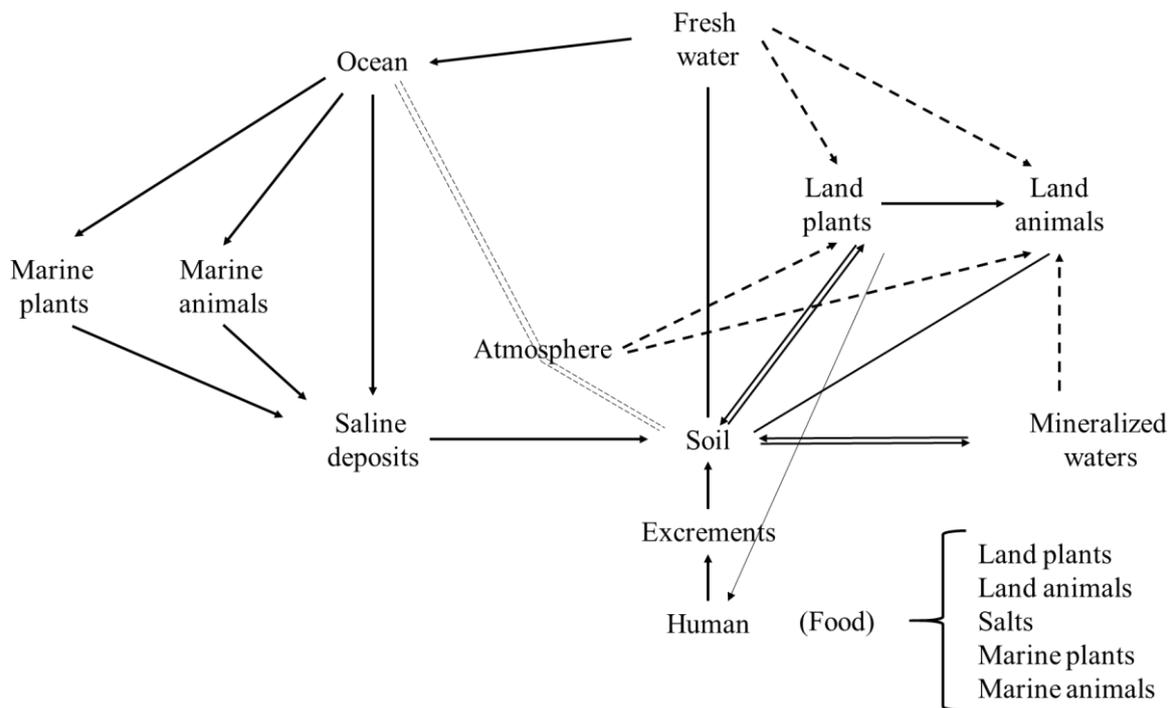


Figure 2.1 – Bromine cycle in nature (*Rosen, 1970*)

The total content of bromine in the earth's crust is relatively small. The main source of the halogen in natural systems is the world's oceans, where there is 30 times more bromine than in the most widespread rock formations of the lithosphere (*Perel'man, 1979*). Bromine is found in large quantities in salt quarries (end products of sea water evaporation), salt lakes and lake brines, highly mineralized reservoir waters and in the waters of oil deposits (*Vinogradov, 1939; Polyansky, 1980; Chemical Encyclopedia, 1988; Emsley, 1991; Ivanov, 1996*). Living organisms and ground evaporation in the hydrosphere play a very important role in the bromine cycle in the nature, since the former concentrate bromine, and the hydrosphere, in its turn, is the depot of industrial accumulations of this element. In addition, increased anthropogenic activity also leads to a significant increase in the content of the element in the environment, which undoubtedly affects its circulation in nature.

Currently, bromine and its compounds are used in numerous areas: the chemical industry, medicine, pharmaceuticals, agriculture, etc. (Table 2.1). Its organic compounds account for about 80% of industrial bromine production (*Yoffe et al., 2013*).

A significant part of the world production of the element was used for the synthesis of dibromoethane, which, together with dichloroethane, used to be used as a component of ethyl liquid, an antiknock additive to auto and aviation fuel (*Polyansky, 1980, Ksenenko, 1995, Greenwood, 2008*). The sharp decline in the use of leaded gasoline, due to environmental legislation, led to a reduction in the production of dibromoethane, which, however, was offset by a significant expansion in other areas of application of the element.

A large proportion of bromine is used to produce methyl bromide (CH_3Br), which is one of the most well-known general pesticides. It is also used for other purposes, for example, as an intermediate in pharmaceuticals. World production of methyl bromide amounted to 48,273 tons in 1985 but had dropped to 24,258 tons in 2009, after a production peak of 70,038 tons recorded in 1995 (*Yoffe et al., 2013*). It is noted that in the 1960s in California, almost 100% of the strawberries grown were cultivated with bromomethane (*Duafala, Gillis, 1999*). It is rather difficult to estimate emissions of

methyl bromide in the environment due to the complexity of its use. Researchers estimated that in 1995 about 24,000 tons of bromomethane came into the environment from its use as a soil fumigant, approximately 13,000 tons from its use as a commodity fumigant (processing of grains and fruits for transportation), 5000 tons - from the use of leaded gasoline, as well as 20,000 from anthropogenic combustion of biomass (Duafala, Gillis, 1999). Since methyl bromide is an ozone depleting substance, its use is currently regulated by the Montreal Protocol (UNEP/UNEP, 1996). In 2005, it was banned for use on the territory of the Russian Federation, but in 2011, under the name "Metabrom-RFO", it was again included in the list and allowed to be used for disinfection of various types of grain products, seeds, etc. (Mordkovich, 2011).

Table 2.1 - Main applications of bromine and its compounds

Activity	Application (example)	References
Chemical industry	- antiknock additive to fuel (<i>ethyl dibromide</i> – $C_2H_4Br_2$); – fire retardants - special additives that reduce the inflammability of various materials: plastic, fibers, etc. ($C_{24}H_{34}Br_4O_4$; $C_{12}Br_{10}O$; NH_4B ; $CaBr_2$; $BrCl$); – paint thinner (<i>ethyl dibromide</i>);	<i>Polyansky, 1980</i> <i>Ksenenko, 1995</i> <i>Greenwood, 2008</i> <i>Yoffe et al., 2013</i>
Chemical industry	– synthetic rubber production; – manufacture of means of water disinfection (<i>benzyl bromoacetate</i> ; $NaBr$; $BrCl$); – chemical analysis (<i>bromoform</i>); – propellant oxidize (BrF_5); – additive to fluorine-containing oxidants, etc	<i>Polyansky, 1980</i> <i>Ksenenko, 1995</i> <i>Greenwood, 2008</i> <i>Yoffe et al., 2013</i>
Agriculture	– common pesticide (<i>methyl bromide</i> ; <i>3-bromo-1-propene</i> ; <i>bromochloromethane</i> ; CF_3Br); – nematicide (<i>ethyl dibromide</i> , <i>methyl bromide</i>)	<i>Ksenenko, 1995</i> <i>Greenwood, 2008</i> <i>Yoffe et al., 2013</i>
Medical/ Pharmaceutical industry	– pharmaceutical preparations and vitamin synthesis (<i>1-bromo-2-phenylethane</i> , <i>bromochloromethane</i> , CF_3Br , $BrCl$, $Br(CH_2)_3Cl$ in the production of <i>fluphenazine</i> , <i>gemfibrozil</i> , <i>trazodone</i> , <i>opipramol</i> . <i>Methyl bromide</i> in the production of <i>clofazam</i> , <i>glycopyrrolate</i> , etc.); – study of the action mechanisms of bromine-containing medications (^{82}Br); – in neuroses, hysteria, increased irritability, insomnia, hypertension, epilepsy and horea ($NaBr$; KBr ; $LiBr$; NH_4B ; $CaBr_2$); – obesity treatment;	<i>Harmful chemicals, 1988</i> <i>Yoffe et al., 2013</i>

Continuation of Table 2.1

Medical/ Pharmaceutical industry	– in ultra-low doses treats endocrine diseases without hormonal drugs; –malignant tumors treatment (^{82}Br)	<i>Harmful chemicals, 1988</i> <i>Yoffe et al., 2013</i>
Food industry	– flour whitener (KBrO_3 ; $\text{Ca}(\text{BrO}_3)_2$); – additive for preserving the consistency of food (<i>brominated oil – E443</i>); – food additive - biotin ($\text{Br}(\text{CH}_2)_3\text{Cl}$)	<i>Yoffe et al., 2013</i>
Nuclear industry	– fluorination of uranium to UF_6 in the processes of obtaining and regenerating nuclear fuel (BrF_3)	<i>Greenwood, 2008</i>
Other	– extinguishing fires in radio and electric equipment (CH_2BrCl ; CF_3Br ; CF_2BrCl); – high-density fluids for drilling fluids (NaBr ; KBr ; CaBr_2 ; ZnBr_2); – in absorption refrigeration and air-conditioning (LiBr); – for the manufacture of photosensitive materials in film and photo industries (AgBr ; NaBr ; KBr ; NH_4Br ; CaBr_2 ; CuBr_2); – in limiting release of mercury to the environment (CaBr_2); –weapons production (warfare agents); –gold and platinum metallurgy.	<i>Ksenenko, 1995</i> <i>Harmful chemicals, 1988</i> <i>Greenwood, 2008</i> <i>Yoffe et al., 2013</i>

Due to such wide human use of bromine and its compounds, the element is redistributed in natural systems, which leads to environmental pollution. It is noted that bromine is found in high concentrations in the sewage waters of chemical-pharmaceutical, petrochemical and mining companies (*Grushko, 1982*), as well as in the drains of firms in the heat-and-power industry (*Ivanov, 1996*). Atmospheric emission of bromine is fixed with various technologies of coal combustion. Studies show that bromine practically does not precipitate in entrails and does not remain in the ash, but enters the atmosphere with water vapor and gases (*Kizilstein, 2002; Yudovich, 2006*). In addition, numerous works have repeatedly shown the increased content of the element in the components of the environment located near enterprises of the thermal power industry, petrochemical production, and the nuclear fuel cycle (*Ecology of the Northern* , 1994; *Shatilov, 2001; Baranovskaya, 2003; Yazikov, 2006; Ecological and geochemical features* , 2006; *Talovskaya, 2008; Zhornyak, 2009; Mezhibor, 2009; Baranovskaya, 2011; Narkovich, 2012;*

Filimonenko, 2015, etc.). High levels of the halogen accumulation are observed in the atmospheric air near roads (*Yatin et al., 2004*), and in the snow cover near the airports (*Zikovsky, 1986*).

In general, it should be noted that bromine has high levels of technogenicity and man-made pressure – 0.1-1 mg/km², as well as one of the highest indicators of man-made use (*Ivanov, 1996*). However, the techno-geochemistry of the element has been studied extremely poorly, and the features of its technogenic concentration in the environment require particular attention.

2.1. Bromine content in the hydrosphere and atmosphere

About 75% of all available bromine is in the hydrosphere, most of it concentrated in the oceans. Bromine occupies the ninth place among the total number of elements found in sea water, in terms of the quantitative ratio in the total salt mass (*Rosen, 1970*). Beginning with M. Balar, who discovered bromine in 1826 in Mediterranean salt brines, there were numerous indications of its presence in sea water. It is not surprising that the content of the element in sea water is one of the most accurately determined constants and amounts to 65-67 mg/l (*Krasintseva, 1968, Rosen, 1970, Polyansky, 1980, Ivanov, 1996*). However, its concentration may vary depending on the source. Since water salinity changes with the climatic zones, bromine content can vary considerably in the same object. The main form of bromine in water is anionic (Br⁻). The Cl/Br ratio is an important genetic indicator for characterizing natural waters (*Vinogradov, 1939*).

An important feature of the element is its high coefficient of water migration, as well as high thalassophilia, i.e. the content in sea water is much higher than the concentration in fresh water (*Ivanov, 1996*). In the latter, the average Br content is about 0.2 mg/l (*Harmful chemicals, 1988*), while in fresh lakes and groundwater it is not more than 0.01 mg/l, and in river waters 0.03 mg/l (*Perel'man, 1979*). Global annual removal of bromine with river flow is at the level of 740 thousand tons (*Harmful chemicals, 1988*). In rivers and underground waters of humid regions, there are lower

concentrations of the halogen in comparison with arid regions, where the largest amount of the element is fixed in salt lakes and solonchaks.

Elevated bromine contents are noted in underground and heavily mineralized waters. As a rule, a direct relationship between the concentration of bromine, calcium and the degree of metamorphism of groundwater is observed. The amount of bromine can increase in parallel with the increase of the total amount of chlorine, as well as with an increase of the total mineralization and depth of aquifers occurrence (*Rosen, 1970*).

Many researchers (*Vinogradov, 1939, Sulin, 1946, Krotova, 1956*) believe that underground highly-mineralized iodine-bromine waters represent highly altered brines of ancient shallow seas. The muddy material of these seas is very rich in the remains of organisms, from which, according to modern understanding, oil was formed. It is also believed that brines of artesian basins in which powerful accumulations of bromine are observed are genetically related to evaporate layers (*Yudovich, 2006*). A clear picture of the prevalence of bromine in the aquatic environment is given in Table 2.2.

Concerning the aerochemistry of bromine, the first mention of it is found in the work of *M. Marchand, (1852)*, who first discovered halogen in atmospheric precipitation (rain). Later data was also obtained about the element in the air of Odessa (*Burkser, 1937*) and in aerosols in Hawaii (*Duce et al., 1963*). It is established that the content of bromine in the air of maritime territories is much higher than in the air of continental regions, due to the transition of the element to the atmosphere together with seawater - about 4 million tons (*Polyansky, 1980*). It is noted that 2500 tons of bromine per year enters the atmosphere as a result of wind erosion of soils; 670 tons per year as a result of volcanic eruptions; 0,5 tons per year with cosmic dust; 20,000 tons per year from forest fires; and 60,000 tons per year from industry and transport (*Ostromogilsky, 1984*).

The processes of the transfer of the halogen from the sea into the atmosphere and its further metamorphism over the continent are of great importance in the aerochemistry of the element (*In the memory of..., 1994*). In the atmosphere, bromine can be in the form of Br^- , Br_2O , BrCl , BrONO_2 , as well as organic compounds (for example, CH_3Br). The contents of bromine in the atmosphere are presented in Table 2.3.

Table 2.2 - Bromine content in the hydrosphere according to the data of different researchers (mg/l)²

Object	Observation point	Content	Reference	Object	Observation point	Content	Reference
Ocean	–	65–67	<i>Vinogradov, 1939</i>	Fresh lakes and groundwater	–	no more than 0,01	<i>Perel'man, 1979</i>
			<i>Krasintseva, 1968</i>				
			<i>Rosen, 1970</i>				
			<i>Polyansky, 1980</i>				
			<i>Ivanov, 1996</i>		lake Baikal	0,2	<i>Shouakar-Stash et al., 2007</i>
Sea water	–	4,6–70	<i>Polyansky, 198</i>	River waters	–	0,001–0,1	<i>Polyansky, 198</i>
	the sea of Azov (depth 0–9 m)	29,9	<i>Krasintseva, 1968</i>		–	0,03	<i>Perel'man, 1979</i>
	the Black sea (depth 0–1000 m)	35,4			–	0,02	<i>Vinogradov, 1939</i>
	the Black sea (depth 0–2000 m)	32,0			the Dnieper river	37,5 γ/l	<i>Krasintseva, 1968</i>
Waters of salt lakes	–	50–800	<i>Polyansky, 198</i>	the Yenisei river	45,8 γ/l		
	–	till 1300	<i>Perel'man, 1979</i>	the Lena river	11,2 γ/l		
Lacustrine brine	–	n* 100 – n*1000	<i>Polyansky, 198</i>	Waters of oil deposits	–	n*100	
							<i>Rosen, 1970</i>
Iodine-bromine waters	–	till 1900	<i>Perel'man, 1979</i>	Waters of oil deposits and other brines	USA (Bradford)	300	<i>Vinogradov, 1939</i>
Strongly mineralized formation water	–	1200	<i>Polyansky, 198</i>		Romania	2–1000	
Weakly mineralized waters of artesian basins	–	5–20	<i>Polyansky, 198</i>		USSR	5–2000	
Deep waters	–	20–4000	<i>Perel'man, 1979</i>		Yugoslavia	0,8–6	
	Siberian platform	2000–8500	<i>Shouakar-Stash et al., 2007</i>		Italy	180	
		6500–12600	<i>Shvartsev et al., 2012</i>		Java	20–80	

² Unless otherwise indicated

At an altitude of 300-1500 m, aerosols are extremely depleted in bromine, which occurs due to photochemical oxidation of bromide to free bromine in the presence of O₂ under the influence of sunlight (*Krasintseva, 1968*).

Table 2.3 – *The content of bromine in the atmosphere according to various researchers (ng/m³)³*

Object	Observation point	Content	Reference
Atmosphere	–	0–1,5 γ/l	<i>Krasintseva, 1968</i>
	South Pole	0,33–1,41	<i>Ivanov, 1996</i>
	Greenland	14–20	
	USA	6–1200	
	Central America	65–460	
	South America	2–200	
	Japan	1,6–150	
	Tokyo	17	<i>Miura, 1990</i>
	Norway	4,4	<i>Ivanov, 1996</i>
	Germany	30–2500	
	Ankara	680	<i>Yatin, 1994</i>
	Athens	130	<i>Scheff, 1990</i>
	Bangkok	41	<i>Chueinta, 2000</i>
	Barcelona	420	<i>Ferrer, 1990</i>
	Budapest	29	<i>Salma, 2001</i>
	Santiago	71	<i>Rojas, 1990</i>
	Chernivtsi	105	<i>Scheff, 1997</i>
	Odessa	23,4 γ/m^3	<i>Burkser, 1937</i>
	Moscow	2,3 γ/m^3	<i>In the memory of..., 1994</i>
	Maximum in cities	1500	<i>Ivanov, 1996</i>
Industrial cities	1300	<i>Saet, 1990</i>	
Atmosphere	Background area of the city	17	
	Suburban background	50	
	Regional background	7	
	Natural background in Western Europe	30	<i>Ivanov, 1996</i>
	Natural background in Western Siberia	4	
	Maritime areas	0,03	<i>Rosen, 1970</i>
	Continental areas	0,002	
Precipitation, mg/kg	0,005		
Precipitation, mg/kg	–	0,004-0,03	<i>Krasintseva, 1968</i>
	–		
	–		
Volcanic exhalations	Kliuchevskaya volcano	0–30 mg/kg	<i>Krasintseva, 1968</i>
	Italy (Stromboli volcano)	4719 mg/m ³	<i>Bichler et al., 1995</i>

Recently, more and more attention has been paid to bromine and its organic compounds in view of their ozone destructive ability. Bromine acts as a catalyst for

³ Unless otherwise indicated

ozone recombination, and, according to various estimates, it accounts for about 15-35% of the destruction of the ozone layer by all halogens (*Smoydzin et al., 2009*).

2.2 About the variability of bromine concentrations in the lithosphere

According to the estimations of different authors, the bromine content in the earth's crust is 1.6 mg/kg (*Vinogradov, 1949*); 2.1 mg/kg (*Vinogradov, 1962*); 2.5 mg/kg (*Goldschmidt, 1937*), which determines about 46-50 places of its prevalence. The Clarke of Br in the earth's crust practically coincides with the clarke of hafnium (2,8 mg/kg), cesium (2,6 mg/kg), uranium (2,3 mg/kg), europium (2,1 mg/kg), and also tin (2,1 mg/kg). Bromine minerals are very rare and are represented by bromargyrite (AgBr), iodobromite ($2\text{AgCl} * 2\text{AgBr} * \text{AgJ}$) and embolite (Ag (Cl, Br)). However, in the form of an isomorphous impurity, the element is found in many minerals and rocks: common salt, silvinit, carnallite, bischofite, biotite, apatite, quartz, etc (*Ivanov, 1996*). The data, presented in Table 2.4, gives a general picture of the bromine content in rocks, soils and other objects.

Soils

The distribution of bromine in soils was first investigated by L.S. Selivanov, thanks to whom the laws of its accumulation were understood (*Selivanov, 1939*). We also find data on the element in the soil cover in the works of A.P. Vinogradov, A. Kabata-Pendias, B.Y. Rosen and many others. A major contribution to the study of bromine (along with other halogens) in the soils of the south of Western Siberia was made by a senior researcher, doctor of biological sciences Konarbaeva G.A. The research data show that the content of bromine in soils usually ranges from 5-40 mg/kg (*Kabata-Pendias, 1989*), according to *Vinogradov (1957)* it is 5 mg/kg. In soils, the element can be in the form of various ions: Br^- , BrO^- , BrO_3^- , BrO_4^- , as a rule elemental bromine does not occur in soils.

Nowadays there is no consensus on the source of soil enrichment with bromine. It is believed that the main sources of the element in soils are volcanic exhalations and sea water. Some authors suggest the enrichment of the upper soil horizons of halogen may be by precipitation (*Kabata-Pendias, 1989*). For example, according to estimations (*In the memory of..., 1994*), the annual amount of bromine added to the soil by precipitation is 24 g/ha. Other researchers point out the significant contribution of plant litter, which may

concentrate a variety of elements necessary to soil microorganisms for the complex biogeochemical transformation processes of organic matter (*Vinogradov, 1957; Harmful chemicals, 1989*). Different ways of Br entering and removing various soil types are possible. For example, in black soils, the dominant entry of the element is from atmospheric precipitations and its removal by surface waters. For solonchaks, entry is due both to atmospheric precipitation and surface and groundwater runoffs, removal by descending gravity solutions (*Konarbaeva, 2008*).

Among a variety of components, the main role in the accumulation of bromine is due to humus (*Selivanov, 1946; Vinogradov, 1957; Rosen, 1970*). Soil humidity also plays a significant role in the accumulation of the element, since they greatly influence the migration rate of the halogen. The works of *G.A. Konarbaeva (2004, 2008)* showed that the soil-forming rocks at the present stage do not play a significant role in the accumulation of bromine, especially for the upper horizons. However, they could serve as sources of the element in the process of their formation. Despite the sorption of bromine by organic matter and clays, it is an element that is easily leached from the soil profile and is released in large quantities into oceanic basins (*Kabata-Pendias, 1989*). Bromine mainly concentrates in zonal types of soils, rich in humus, and in intrazonal soils, enriched with finely dispersed mineral particles and possessing an alkaline reaction. Its maximum concentrations are found in solonetztes, while the minimum concentrations are found in sod-podzolic soils (*Konarbaeva, 2001*), as well as in forest and gray soils, which are usually poor in bromine due to their low content of organic matter (*Kabata-Pendias, 1989*).

Peat

In the pre-war years, *LS. Selivanov* showed that bogs are particular bromine biogeochemical provinces (*Selivanov, 1939*). The content of bromine in peat is usually higher than in soils and can reach 100 mg/kg (*Bernatonis et al, 1989*), but the data on the form of the element is still poorly understood. There is information that bromine in peats can be primary-vegetative Br_{bio} , which is found in plants as a strong, slightly soluble in water compound. However, the presence of sorption bromine Br_{sorb} is also not excluded (*Yudovich, 2006*). The element can enter peat bogs as part of atmospheric precipitation.

Br in peat is unevenly distributed, and its concentrations vary depending on the type of peat deposits: the smallest content is observed in upland peat, 10.5 mg/kg, and the largest, in lowland peat, 33.8 mg/kg (*Bernatonis et al., 1989*). It should be noted that an increase in bromine concentrations can be observed both with depth and in the upper layers.

Coal

The first studies of the element in coals were made in Germany in the 1930s, but subsequent data only appeared 30 years later (*Yudovich, 2006*). Existing geochemical data suggest that the element is typomorphic for coals (*Yudovich et al, 1985*). Enrichment of coal with halogen is associated with the vegetation from which they are formed, plus the impact of the sea and volcanic activity. There are several forms of Br in peats: mineral (Br_{min}), sorbed (Br_{sorb}) and organic (Br_{org}). Considerable data indicates that the latter is dominant (*Yudovich et al, 1985, Kler et al, 1987*). It is noted that the presence of Br_{org} can be associated not with the organic matter itself, but with the components of sorption ash. The average bromine content in coals is 5.2 mg/kg (*Yudovich, 2006*). However, the concentration and occurrence form of the element can vary both in thermal epigenesis and in the hypergenic oxidation of coals. The research data also shows the relationship between levels of bromine accumulation and coal metamorphism: Br content in lignites is 14 mg/kg, in sub-bituminous coals - 16 mg/kg, and in bituminous coals - 67 mg/kg (*Yudovich, 2006*).

Oil

At present, there is insufficient information on the prevalence and forms of bromine in crude oil, and even less in commercial petroleum products. For example, in impurities of crude oil in West Siberia, bromine was detected only in 8 out of 24 samples, and its content varied from 1.6 to 14 mg/kg (*Begak et al., 2001*), while in Libyan crude oil the figure was 0.65 mg/kg (*Shah et al, 1970*). In diesel fuel and in gasoline (Belgium) 32 mg/g and 250 mg/g of bromine was found respectively (*Block et al., 1978*).

Table 2.4 - Bromine contents in the lithosphere objects (mg/kg)

Object		Observation point	Content	Reference	Object	Observation point	Content	Reference	
<i>Rocks</i>					<i>Soils</i>				
Magmatic	Ultrabasic	–	0,2–1,0	<i>Kabata-Pendias, 1989;</i> <i>Kabata-Pendias, 2011</i>	In general	–	5–40	<i>Kabata-Pendias, 1989</i>	
	Basic	–	0,5–3,0			–	5	<i>Vinogradov, 1957</i>	
	Intermediate	–	1–4			Western Siberia	0,03–59,7	<i>Konarbaeva, 2004</i>	
						Great Britain	10–515	<i>Kabata-Pendias, 1989</i>	
	Acid	–	0,3–4,5			Japan	3–495	<i>Yuita, 1983</i>	
	Acid volcanic	–	0,2–1,0			USA	5,6	<i>Shacklette, 1984</i>	
Sedimentary	Argillaceous sediments	–	5–10	<i>Own study</i>	Podzols	–	1,9	<i>Rosen, 1970</i>	
	Shale rocks	–	6–10		Forest gray	–	5,7		
	Sandstones	Verkhnekamskoye deposit	1–5		15–20	Black	–		8,0
			11–17			11–17	Chestnut		–
	Limestones, dolomites	–	6		<i>Kabata-Pendias, 1989</i>	Gray	–		9,8
	Clay and shale	–	4–8		<i>Krasintseva, 1968</i>	Red	–		7,0
			6		<i>Perel'man, 1989</i>	Silts	–		62
In general	–	7	<i>Krasintseva, 1968</i>	–	2,5		<i>Vinogradov, 1950</i>		
Crystalline	–	2,1	<i>Krasintseva, 1968</i>	Peats	–	11,5-56,5	<i>Selivanov, 1946</i>		
		1,7-5	<i>Polyansky, 1980</i>		–	30	<i>Perel'man, 1979</i>		
Volcanic	–	5,5	<i>Krasintseva, 1968</i>		Tomsk region	1,4–104,9	<i>Bernatonis, 1989</i>		
Stony meteorites	–	1,5	<i>Polyansky, 1980</i>		Italy	16,3	<i>Ntahokaja, 1995</i>		
		0,6-56	<i>Rosen, 1970</i>		Finland				
Carnallite	Verkhnekamskoye deposit	2200-3400	<i>Own study</i>		Irland				
Rocksalt		34–775			Kuznetsk Basin (ash)	42,5	<i>Rare elements in coals , 2000</i>		
Sylvinitite		58–551		Belgium		23		<i>Vassilev et al., 2000</i>	
Travertin	Pamukkale	Turkey	1	<i>Mongolina, 2011</i>	Coal	Bulgaria	1330		
	Talovskiye chashi	Tomsk region	21,2			Ukraine	1620		
	Vichy	France	6–36						

2.3. Bromine in living organisms

Despite the constant presence of bromine in all living organisms, for a long time the question of its essentiality has not been clearly established, primarily because of insufficient knowledge of its biological role. In the existing classifications of chemical elements, there is no consensus about the physiological role of this halogen. According to the classifications of A. Leninzher (1985), P. Aggett (1985) and V. Mertz (1982), it is obvious that bromine is not an element that plays a vital role in organisms. V.V. Kovalsky (1974) classifies the element as relatively necessary, noting that its biological role can be seen. From the biogenic classification of A.V. Bgatov (1999) it also follows that bromine is one of the relatively essential elements. According to Avtsyn *et al.* (1991), Br is an element that is constantly determined in animal organisms, the significance of which has not been adequately studied. The essentiality of the element was discussed by M. Anke (2001).

In addition, A.I. Perelman paid attention to the location of bromine in the periodic table of D.I. Mendeleev, according to which it is "surrounded" by elements, which play an important role in the physiology of living organisms and are extremely unevenly distributed in landscapes (Figure 1.1), that is a reason for various biogeochemical anomalies. In addition to pointing out the high biophilicity index of bromine, comparable to chlorine and phosphorus (0.75), the author also hypothesized about the important biogeochemical role of bromine in the evolution of the nervous system (Perel'man, 1979).

The recent discovery of American scientists (McCall *et al.*, 2014) shone the final light on the question of the essentiality of the element. The results of studies of Vanderbilt University (USA) showed that, without bromine, collagen molecules of type IV, which play an important role in maintaining the integrity of epithelial and endothelial cell membranes, cannot communicate properly with each other to form a

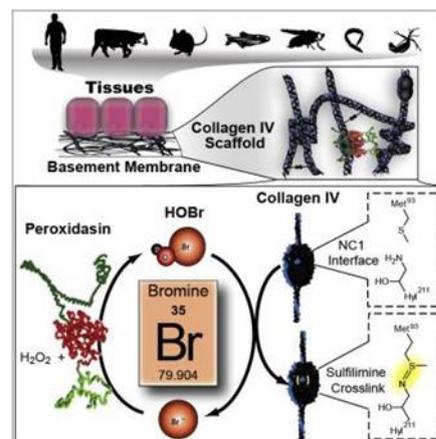


Figure 2.2 - Role of bromine as a cofactor in the formation of IV collagen type (McCall *et al.*, 2014)

structural protein of connective tissue, which can lead to disruption in its development (Figure 2.2). During the experiment, it was shown that bromine is essential for all living organisms, without exception. "Without bromine, there is no life. This is a discovery"- concluded the lead author of the study, Professor Billy Hudson.

Bromine content in plant and animal organisms

According to V.I. Vernadsky, from the total amount of bromine present in the earth's crust, 1/100 of it is associated with living matter, with millions of tons of the element being involved annually in biological migration. According to the absorption intensity by biomass, the halogen refers to the I group of substances, since its concentration in ash is greater than in the earth's crust (*Harmful chemicals, 1988*).

Marine plants and animals are characterized by higher levels of halogen accumulation than terrestrial ones. Some algae, including freshwater, are able to accumulate concentrations of the element 80,000 times higher than in the surrounding aquatic environment. Various biological active bromine-containing compounds were isolated from red algae (*Saenko, 1992*). According to *Ivanov (1996)* the amount of bromine in terrestrial plants varies from 0.002 to 120 mg/kg, whereas according to *Kabata-Pendias(1989)* natural concentrations of the halogen in terrestrial plants do not exceed 40 mg/kg, and higher contents may indicate a contamination. *V.A. Filov (Harmful chemicals, 1989)* notes that the amount of bromine in the phytomass of the continents is about 9 million tons. It has been established that there is more bromine in the leaves of plants than in their roots, while the concentration of the element does not depend on its content in the soils, nor on the type of soils, nor on the pH value. However, it is interesting that plants easily extract from bromine- enriched soils, but the method of its transfer is not yet known. The role of air intake of bromine in plants has not been studied extensively, but some authors note its intake with atmospheric air (*Harmful chemicals, 1988*). The element changes its occurrence forms while accumulating in plant cells: instead of inorganic salts, found in soils and waters, in plants it occurs in the form of complex organic compounds (*Rosen, 1970*).

Element concentrations in mammalian organisms vary widely: from 6 mg/kg in terrestrial animals to 1000 mg/kg in marine ones (*Ivanov, 1996*). It is noted that in the mammalian organism there is no «depot» where bromine is concentrated (*Verkhovskaya, 1962*). The study of the forms of the chemical existence of the element shows that in animal organisms bromine can be in ionic and protein-bound forms, as well as in the form HBr and various bromine-organic compounds (*Verkhovskaya, 1962, Rosen, 1970*). The results of the studies show that high bromine levels can be observed in the thyroid gland of animals, as well as in the pituitary gland, where the halogen content is not constant (*Voinar, 1960*).

In general, the study of the peculiarities of the accumulation of bromine in animal organisms demonstrates the same nature of its distribution, levels and a range of fluctuations in the organs and tissues of various mammals (*Verkhovskaya, 1962*).

Detailed levels of bromine in animals and plant organisms were shown by a number of authors, both Russian and foreign: A. Vinogradov, L. Selivanov, A. Simorin, A. Neufeld, A. Damien, S. Blainan, H. Hofmann, I. Verkhovskaya, A. Kabata-Pendias, B.Y. Rosen and many others. Table 2.5 provides a brief overview of the content of bromine in animals and plants.

Table 2.5 - Bromine content in plants and animals, mg/kg

Object	Observation point	Content	Reference
Microorganisms of mineral springs	the Baikal rift zone	3,9–17,4	<i>Perminova, 2013</i>
Land plants	–	9,5–19	<i>Polyansky, 1980</i>
	–	1–276	<i>Baranovskaya, 2011</i>
Sea plants	–	up to n000 of dry weight	<i>Kabata-Pendias, 1989</i>
	–	203–1004	<i>Saenko, 1992</i>
Seaweed	–	0,01–1000 of dry matter	<i>Rosen, 1970</i>
Algae, kelp	–	400 on live weight	<i>Perel'man, 1979</i>
Sponge	–	up to 2500 of dry weight	
Sea animals	–	60–1000	
Land animals	–	6	<i>Ivanov, 1996</i>

Continuation of Table 2.5

Object	Observation point	Content	Reference
Coelenterates	–	0,11–0,354	<i>Voinar, 1960</i>
Worms	–	0,0195	
Tunicates	–	0,05–0,22	
Mollusks	–	0,05–0,22	

Bromine in the human body

Like animals, there is no specific organ-concentrator of bromine in the human body (*Verkhovskaya, 1962*). The element enters the body, mainly with food, drink and air and is concentrated in various organs and tissues (*Verkhovskaya, 1962; Polyansky, 1980*). According to *V.V. Ivanov(1996)* a human body receives about 7.5 mg of bromine per day, according to *J. Emsley (1991)* - from 0.8 to 24 mg; excretion occurs mainly with the urine - 7 mg according to *V.V. Ivanov (1996)* and 1-2.5 mg according to *A.I. Voinar (1960)*. A small amount of the element can also be eliminated with feces, with saliva and milk, and possibly with gastric juice. The rate of bromine excretion depends, to a considerable extent, on the chloride content in the body: with a low content, bromine accumulates and its excretion in urine decreases (*Avtsyn et al., 1991*). The total content of Br in the body is about 200 mg, with 170 mg in soft tissues. The absorption of the halogen from the gastrointestinal tract is 1, the threshold of renal permeability is 0.1 mg%. The average period of excretion of bromine from the body is 10 days (*Ivanov, 1996*). It is noted that bromine is retained in the blood for a rather long time and is effectively not included in the exchange (*Harmful chemicals, 1988*).

The Br content in the body is not associated with sex, nor with age characteristics (*Verkhovskaya, 1962*). Elevated levels are usually noted in the thyroid gland, slightly less in the blood. However, in the gastric mucosa and the medulla of the kidneys, the amount of this element can sometimes be higher than in the thyroid gland. The average content of halogen is specific for such organs as liver, spleen, adrenal glands, cortical layer of the kidneys, peripheral nerves and pituitary gland. The liver is the main organ in which the destruction of complex organic bromine compounds such as, for example

α -bromine, is observed. Low amounts of the element are found in various parts of the central nervous system. The content of bromine in the pituitary gland is lower than in the blood, but higher than in other parts of the brain. The lowest bromine content was recorded in skeletal muscles (*Voinar, 1960*). According to *P. Quittner (1970)* and *U.E. Saet (1990)* bromine is one of the most common elements in the hair, where it can accumulate in fairly high concentrations. More detailed information on the peculiarities of the accumulation of bromine in the organs and tissues of the human body is presented in Table 2.6.

There is information that during acute attacks of rheumatic fever in children, the amount of bromine in the blood increases, whereas when the condition improves, its level decreases (*Verkhovskaya, 1962*). In addition, it is noted that the normal content of bromine in the blood decreases significantly at certain stages of manic-depressive psychoses.

With the introduction of bromine compounds for therapeutic purposes, its content in the blood, as well as in other tissues and organs, increases and can reach quite high values. Bromine, used for such purposes, is only slowly removed from the body. For example, with a single injection of bromide salts, the highest level of bromine in the blood is observed after 2-3 hours and persists for 48-120 hours, the subsequent decrease may not be achieved for 19 days.

2.3.1 Bromine in food products

Since most bromine enters the body with food (*Voinar, 1962, Verkhovskaya, 1962*) and because the element finds applications in the food industry (see Table 2.1), the study of its accumulation seems to be very important. Unfortunately, in the Russian literature sources, information on the content of the element in food items is extremely poor, more detailed information is available in the works of foreign authors, but this data is not exhaustive.

Table 2.6 - Bromine content in the human body, mg/kg

Object	Observation point	Content	Reference	Object	Observation point	Content	Reference	
Blood	–	4,7	<i>Emsley, 1993</i>	Cerebrum		0,5–1,7	<i>Ivanov, 1996</i>	
	–	1,6–15	<i>Voinar, 1960</i>		the core of the CNS	–	0,076 mg/g	<i>Zheng et al., 1992</i>
	–	1,1–20	<i>Verkhovskaya, 1962</i>		Mitochondria	–	< 0, 030 mg/g	
	–	2,7	<i>Ivanov, 1996</i>		Myelin	–	0,187 mg/g	
	Uzbekistan	18	<i>Zhuk et al., 1988</i>		Synaptic	–	< 0,0321 mg/g	
	Bangladesh	1,1	<i>Khan, 1980</i>			–	10	<i>Roslyakov, 1983</i>
Hair	–	0,2–20	<i>Quittner, 1970</i>	Heart				
	–	5,0	<i>Roslyakov, 1983</i>		Anapa (ash)	78,8	<i>Own study</i>	
	–	0,65–53,3	<i>Ivanov, 1996</i>	Spleen	–	20	<i>Roslyakov, 1983</i>	
	–	12,5	<i>Human. Medico-biological data.</i>		–	9–15	<i>Voinar, 1960</i>	
	Tomsk region	13,3	<i>Narkovich, 2012</i>	Kidney	–	6,7	<i>Ivanov, 1996</i>	
	Western Siberia	2,7 – 13	<i>Baranovskaya et al., 2015</i>		–	10	<i>Roslyakov, 1983</i>	
	–	2,37 ± 0,7	<i>Saet, 1990</i>	Bones	–	7	<i>Ivanov, 1996</i>	
	Poland	2,7			–	38		
	Belgium	3,0			–	6,7		
	USA	8,0		Muscles	–	7,7	<i>Emsley, 1993</i>	
	Canada	0,2–21			–	30	<i>Roslyakov, 1983</i>	
	South Korea	3,5		Lungs	–	7,5	<i>Ivanov, 1996</i>	
	Japan	7,0	–		390			
	Russia	3,59 ± 2,33	<i>Zaichick, 2010</i>	Aorta	–	20–25	<i>Voinar, 1960</i>	
	Taiwan	8,44 ± 2,16	<i>Chiu et al., 2011</i>	Adrenal glands	–	14–18		
World summary	0,0045–880	<i>Zaichik, 2004</i>						
Thyroid gland	–	7,7	<i>Verkhovskaya, 1962</i>	Ovary	–	5,1	<i>Ivanov, 1996</i>	
	–	0,9–1,4	<i>Voinar, 1960</i>	Nails	–	9–10		
	–	10	<i>Roslyakov, 1983</i>	Prostate	–	360		
	–	3	<i>Ivanov, 1996</i>					
Liver	–	6–7,5	<i>Voinar, 1960</i>	Teeth	–	1,1–34		
	–	10	<i>Roslyakov, 1983</i>					

It is worth noting that today in Russia there are no regulatory standards for bromine in food, as described in more detail in the section "*Hygienic standards*". According to WHO standards, the daily allowable dose of bromine consumption is 1 mg per day per 1 kg of body weight. However, as shown in the data studied, consumption of bromine in different countries of the world exceeds this limit (Table 2.7).

Table 2.7 - Daily consumption of bromine with food in different countries (mg/kg/day)

Country	Br, mg/kg/day	Daily allowable dose (WHO)	Reference
Germany	2,5	1	<i>Hou, 1997</i>
China	5,4		<i>Mannan, 1992</i>
	2,28		<i>Hou, 1997</i>
the Netherlands	8		<i>Van Dokkum, 1989</i>
Pakistan	4,74		<i>Hou, 1997</i>
USA	2-8		<i>WHO, 1971</i>
Turkey	2,71		<i>Hou, 1997</i>
Ukraine	3,5		<i>Shiraishi, 1999</i>
Japan	11,4		<i>Matsuda, 1994</i>
	8-12		

The main source of the element's intake into the human body is sodium chloride (*Verkhovskaya, 1962*); methyl bromide and other organic bromine compounds, used for fumigation of soil, grain and fruits, can also be a serious source of its penetration into the human body (*Kabata-Pendias, 1989*). It is established that the effect of the element on different plant species is not the same. For example, potatoes, spinach, sugar beets are sensitive to bromine effects, whereas carrots, tobacco, tomatoes, celery and melons can accumulate a large amount of the element without any visible effects.

Polyansky (1980) notes that food can contain from 0-260 mg/kg of bromine. The published literature data presented in Table 2.8 shows the content of bromine in foods, consumed by people from different countries.

In addition to Br intake with food, other lifestyle aspects, such as smoking, are also important. In tobacco, the increased content of the element is noted. For example,

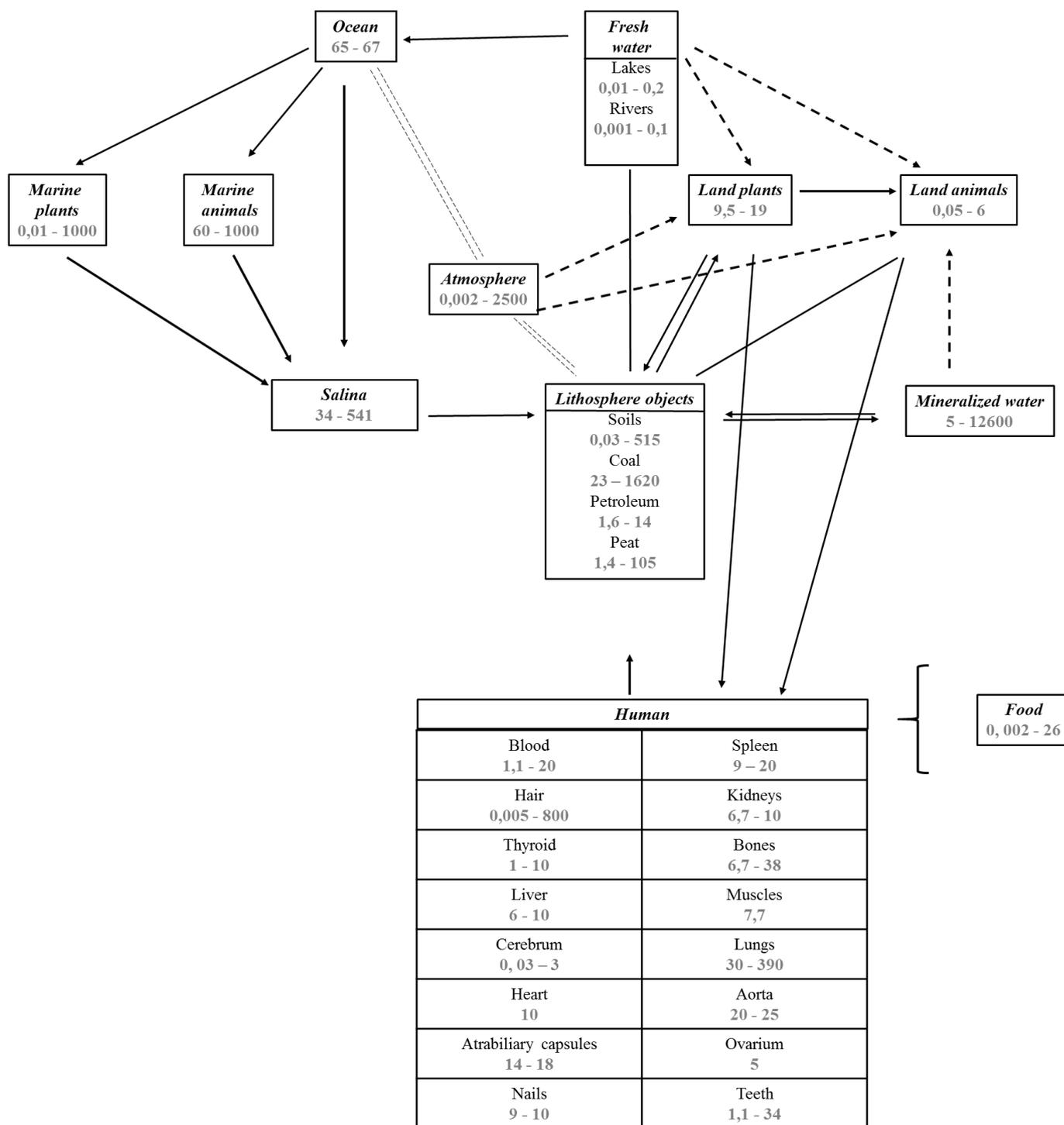
in tobacco in Finland, an average 110 mg/kg of bromine was found, with a maximum of 200 mg/kg, in the solid particles of cigarette smoke - 1 µg/cig, in the gas phase - 5 µg/sig. (*Hasanen et al., 1990*). In Indian tobacco, 110-165 mg/kg of bromine was found (*Mishra, 1983*), in the United States tobacco from 36 to 154 mg/kg (*Nadkarni, 1969*), in Iranian tobacco - 108 to 206 mg/kg (*Abedinzadeh, 1973*), Egyptian - 158 mg/kg, and in the ash of the same cigarette - 481 mg/kg (*Iskander, 1985*). It is noted that the permissible level in tobacco should not exceed 250 mg/kg (*Ahmad et al., 1979*)

2.4 General regularities of bromine accumulation and distribution in the components of the biosphere

A review of the literature data demonstrates that the distribution of bromine in the components of the biosphere (Figure 2.3) is non-uniform. For natural systems, in terms of the degree of bromine concentration, the following series can be represented: in first place, there are the components of the hydrosphere with the maximum element content in the mineral waters - up to 12,600 mg/l. In second place there are coals, in which the concentration of the element reaches 1620 mg/kg. Marine plants and animals are next with a maximum Br content of 1000 mg/kg.

Table 2.8 - Bromine content in food, mg/kg

Food item		Content	Country	Reference	Food item		Content	Country	Reference
Dairy products	milk	2,57	Ukraine	Ko, 2006	Vegetables	<i>in general</i>	3,00	China	Hou, 1997
		3,70	Japan			<i>beetroot</i>	0,15 ± 0,02	–	Gunther, 1966
		1,73	China	Hou, 1997		<i>cabbage</i>	5,3 ± 0,5	Pakistan	Waheed, 2003
		10,3 ± 0,9	Pakistan	Waheed, 2003		<i>cauliflower</i>	6,4 ± 0,6		
		3,6	–	De Vos, 1984		<i>broccoli</i>	0,13 ± 0,01	–	Gunther, 1966
Eggs		5,51	China	Hou, 1997		corn	0,51 ± 0,02	–	
		7,3 ± 0,5	Pakistan	Waheed, 2003			0,9–1,7	–	Kabata-Pendias, 1989
Meat	<i>in general</i>	4,18	China	Hou, 1997		cucumber	10-20	–	Gunther, 1966
	<i>beef</i>	0,83 ± 0,07	Pakistan	Waheed, 2003			9,91 ± 0,05	–	
	<i>mutton</i>	0,58 ± 0,05				0,18 ± 0,01	–		
	<i>hen</i>	1,3 ± 0,1			2,4 ± 0,2	Pakistan	Waheed, 2003		
Sea food		7,83	China	Hou, 1997	pepper	0,18 ± 0,01	–	Gunther, 1966	
<i>in general</i>	1,59	7,33 ± 0,94				Egypt	Awadallah, 1986		
Cereals	barley	0,34 ± 0,02	–	Gunther, 1966	tomato	10,3 ± 0,1	Pakistan	Waheed, 2003	
		2,1–6,4	–	Kabata-Pendias, 2011		10	–	Kabata-Pendias, 2011	
	wheat	2,41	Iran	Pourimani, 2013	radish	0,10 ± 0,01	–	Gunther, 1966	
		6,71	Saudi Arabia	Al-Dayel, 2002		7,7 ± 0,6	Pakistan	Waheed, 2003	
		12,5	India	Kulkarni, 2009		24–26	–	Kabata-Pendias, 1989	
		8,04	USA	Iskander, 1986a	zucchini	0,13 ± 0,01	–	Gunther, 1966	
		0,80 ± 0,08	Pakistan	Waheed, 2003		turnip	6,6 ± 0,6	Pakistan	Waheed, 2003
	rice	0,64 ± 0,06			eggplant	24,2 ± 1,7	Pakistan		
oat	3,1	–	Kabata-Pendias, 2011	3,78 ± 0,26	Egypt	Awadallah, 1986			
Fruits	<i>in general</i>	0,16	China	Hou, 1997	potato	2,19	China	Hou, 1997	
		1,1	Jamaica	Howe, 2005		1,3 ± 0,1	Pakistan	Waheed, 2003	
		0,7	England			3,92 ± 0,23	Egypt	Awadallah, 1986	
	orange	0,04	–	Kabata-Pendias, 2011		4,2–14,3	–	Kabata-Pendias, 1989	
	apple	0,002	–			2,7–14,2	–	Voinar, 1960	
Sugar	0,44	China	Hou, 1997	beans	1,91	China	Hou, 1997		
Wine	0,06			0,57	Jamaica	Howe, 2005			
Bread	0,9–6,1	–	Voinar, 1960	dill	3,70 ± 0,19	Egypt	Awadallah, 1986		



Human	
Blood 1,1 - 20	Spleen 9 - 20
Hair 0,005 - 800	Kidneys 6,7 - 10
Thyroid 1 - 10	Bones 6,7 - 38
Liver 6 - 10	Muscles 7,7
Cerebrum 0,03 - 3	Lungs 30 - 390
Heart 10	Aorta 20 - 25
Atrabiliary capsules 14 - 18	Ovarium 5
Nails 9 - 10	Teeth 1,1 - 34

Figure 2.3 - Simplified scheme of the bromine distribution in the environment within its natural cycle, according to the literature review, in mg/kg (for hydrosphere objects in mg/l, for the atmosphere in ng/m^3)

The human body, according to the concentration of halogen, is in fourth place, and not at the end, as the food chain suggests. The maximum bromine content, with its sharp variability, which determines this position, is observed in the hair. The next

media are terrestrial plants and animals. The lowest contents of the element are observed in river water (from 0.001 mg/l) and atmospheric air (2500 ng/m³).

Brief conclusion of chapters 1 and 2

From the geoecological point of view, bromine is undoubtedly of particular interest. The element is characterized by high chemical activity and migration ability, which largely determines the characteristics of its behavior in the environment. The biological effect of bromine is ambivalent: on the one hand, the element is essential, on the other, it can be extremely toxic, having a negative effect on the most important physiological functions of living organisms and participating in the development and formation of certain diseases. The question of the technogenesis of bromine and the features of its technogenic concentration in various components of the environment also require serious attention.

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CHAPTER 3. WAYS OF ASSESSING THE ECOLOGICAL STATE OF THE ENVIRONMENT

Societal development is characterized by a high negative impact on the environment, which results in a disruption of the dynamic equilibrium and sustainability of natural systems, and an imbalance of their interaction and functioning. In turn, this has led to a deterioration in environmental quality and people's living conditions (*Saet et al., 1990; Abdullin et al., 2009; Grobe et al., 2009; Tegako, 2013; Chelnokov et al., 2015, etc.*). Today, in some regions of Russia and other countries the ecological situation is unfavorable and pollution level is high, sometimes critically high (*Mage et al., 1996; Keller, 1998; Mayer, 1999; Kvashnina, 2001, etc.*). In addition, there is a clear connection between the increase of environmental pollution and increased morbidity (*Ecology of the Northern , 1994, Senotrusova, 2005; Sukhikh, 2005; Ecological and geochemical features , 2006; Air quality , 2009; Vitrishchak et al., 2010; Clarke et al., 2010; Ovsyannikov et al., 2011; Sosunova, 2013; Lee et al., 2014; WHO, 2016 et al.*). Complex ecological tensions necessitate the development of measures aimed at minimizing the negative impact on the environment. However, to make effective decisions, a clear understanding of the methods / approaches / concepts / models available for assessing the ecological status of the environment is necessary, since there is no single, commonly agreed gradation and structure of them.

The main criteria of environmental quality in Russia and abroad are ***the environmental and hygienic standards*** (*Isidorov, 1997; Egorova, 2003; Yazikov, 2003; Moeller, 2005; Essential environmental health standards ..., 2008*), which are regarded as a guarantee of public health and environmental safety (*Alexandrova, 1990*). It is interesting to note that the first mentions of anthropogenic impact on the natural environment were found in ancient Babylon and India (*Pavlov, Peshkova, 2006*). However, the legal system in the form of decrees and laws, regulating the permissible anthropogenic load, was formed only at the beginning of the 20th century. The valuation concept was developed first in the USSR, and then in the United States and other countries (*Alexandrova, 1990*).

Environmental quality standards are established, in general, to ensure environmental well-being: the preservation of natural ecosystems, genetic funds of

plant and animal populations, and other organisms, as well as to protect human health (*Pimenova, 2009*). These include: standards for maximum permissible concentrations (MPC) and maximum permissible level (MPL). Recently, instead of MPC and MPL, the term "maximum allowable level" is widely used. The standards of permissible impact on the environment are established in accordance with the economic impact indicators and other activities, in compliance with environmental quality standards. These include: the maximum permissible emissions (MPE) and maximum permissible discharges (MPD) and temporarily agreed emissions and discharges. Moreover, as it is shown in the study of *Z. I. Zholdakova and O.O.Sinitsina (2004)*, there is a high correlation between Russian and foreign standards, which indicates unity of the fundamental principles of standardization of chemical elements and substances at the international level.

Despite the widespread application of environmental and hygienic standards, they have been subjected to serious criticism, which began almost immediately after their legal approval (*Bashtan et al., 1941; Pavlov, Peshkova, 2006*). Among many shortcomings of the system of environmental regulation, we highlight just a few: 1) the lack of maximum permissible concentrations of pollutants (MPC) and other standards for some components of the environment and food; 2) lack of consideration of multifactor effects of chemicals, i.e. different ways of their penetration routes (with air, food or through the skin). Another disadvantage in the environmental regulations, in our view one of the most significant, is the lack of the spatial-geographical differentiation of the territory, i.e., they do not take into account its natural features (natural background, climate, etc.). It is widely known that the behavior of chemical elements in different areas is not the same, and this determines their effect on living organisms (*Limanova, 2015*). This is especially true for areas with an excess or a lack of certain chemical elements, as well as for areas with strong anthropogenic interference, where there is a significant redistribution of chemical elements in all components of the environment and a change in their natural background concentrations. Thus, we can conclude that all of the above-mentioned disadvantages

can, to some extent, limit the use of this method as a basic tool of environmental assessment.

A common method of assessing the state of the environment is research based on the chemical analysis of individual components of the environment, and the tissues and organs of living organisms (*Kovalsky, 1974; Glazovskaya, 1988; Saet et al., 1990; Alekseenko, 2006; Ecological and geochemical features et al., 2006; Yazikov et al., 2010; Strakhovenko, 2011; Baranovskaya et al., 2015*). They may have different names: geochemical, ecological-geochemical investigations or monitoring, etc., but, in fact, they all represent the same approach to the study of the environment. However, if in the context of geochemical/ecological-geochemical research it is possible to study the individual components of the environment, monitoring means a complex study, i.e. the totality of natural objects (*Yazikov, 2006*). It is also worth noting that in the foreign studies, we do not find the term “geochemical and ecological-geochemical studies”, these works, in general, refer to “environmental monitoring”.

A major contribution to the development of this field in Russia was made by Y. A. Saet, based on the existing work of V. I. Vernadsky, A. P. Vinogradov, V. V. Kovalsky. Important studies were also made by A. I. Perelman, V. V. Ivanov, M. A. Glazovskaya, V. A. Alekseenko, employees of the Scientific Research Institute of Hydrogeology and Engineering Geology, the Vernadsky Institute of Geochemistry and Analytical Chemistry of Russian Academy of Sciences, Institute of Mineralogy, Geochemistry and Crystal Chemistry of Rare Elements, Institute of Geochemistry of A. P. Vinogradov, etc. (*Yazikov, 2006*).

The environment is the research object in environmental-geochemical/geoecological studies, and the changes it undergoes under the influence of natural and anthropogenic factors at various levels: from local to global (*Rožanov, 2015*). The main goal is to study the patterns of distribution, migration and concentration of chemical elements in the environment, in natural and technogenic landscapes, to identify spatio-temporal features of the distribution of chemical elements and interrelationships of human activities with the environment, etc. (*Saet et*

al., 1990; *Timashev*, 2007). The general methodological principles of carrying out these studies are reflected to the fullest extent in the study of *E.G. Yazikov* (2006).

Ecological-geochemical/geoecological research is based on an interdisciplinary approach, i.e. the scientific and methodical basis of various sciences: biology, physics, ecology, chemistry, landscape science, geography, etc. Therefore a significant number of different analytical, mathematical methods of analysis, mapping methods, ecological modeling, GIS technologies and many others could be used (*Gagina*, 2002).

Such studies are widely used to study the impact of industrial enterprises on the environment (*Rikhvanov*, 1997; *Ecology of the Northern ...*, 1994; *Kurolap*, 1998; *Baranovskaya*, 2003; *Yazikov*, 2006; *Zhornyak*, 2009; *Li et al.*, 2009; *Nadal et al.*, 2009; *Wei et al.*, 2010; *Nadal et al.*, 2011; *Baranovskaya*, 2011; *Vorobyova*, 2015; *Filimonenko*, 2015; *Yalaltdinova*, 2015), and the ranking of territories to identify territorial differences in the degree of environmental tension (*Atlas ...*, 1995; *Gamm*, 2004; *Kirillov*, 2011; *Dubrovskaya*, 2014; *Ermolaeva et al.*, 2014; *Regions and cities of Russia ...*, 2014).

However, practice shows that there is increasing interest in studies focusing not simply on ranking territories in accordance with their ecological state, but, primarily according to the degree of their environmental sustainability with the application of aggregated integrated indicators (*Bakumenko*, 2008). As an example of the use of environmental indicators at the international level we can cite the ***Living Planet Index***, used to assess the state of natural ecosystems. Within this index, several indicators are measured: the natural capital of forests, aquatic ecosystems, etc., each of which reflects the change in the population in the ecosystem. Another example is the *Environmental Sustainability Index*, covering over 20 factors that can affect environmental sustainability (air quality, water, emissions and waste reduction, natural resource management, etc.). A number of studies on this subject have also been conducted in Russia (*Ayvazyan et al.*, 2006; *Shikhova*, 2007; *Bakumenko*, 2008, etc.). In addition, at the national level, in the context of the "Concept of the transition of the Russian Federation to sustainable development", a system was established based on official

statistics, including 42 indicators of which 21 consider ecology (atmosphere, biodiversity, fresh water, etc.). However, this system is not yet widely used due to the lack of broad regional databases.

Analyzing the experience of European countries (*Starostina, 2013*), we can conclude that all the methods aimed at environmental assessment, can be divided into two categories: procedural and analytical. The first include methods that consider social and economic aspects, along with environmental ones. This group includes: Environmental Impact Assessment (EIA), Strategic Environmental Assessment (SEA), as well as the Environmental Management System (EMS). The second category of methods focuses primarily on the technical issues and includes: Material flow analysis (MFA); Substance flow analysis (SFA); Environmental Risk Assessment (ERA), Cost-benefit analysis (CBA) and Life Cycle Assessment (LCA).

In addition, in our study (*Perminova et al., 2016*), it was also found that all the above methods, along with several additional ones (Ecological Footprint, etc.) are often used in the framework of systematic environmental analysis not only within the countries of the European Union, but all over the world. At the same time, there are only four methods which are the most frequently used. These will be considered more in detail: Environmental Impact Assessment, Ecological Footprint, Material Flow Analysis and Life Cycle Assessment.

Environmental Impact Assessment (EIA) is a method aimed at assessing the degree of influence of any type of planned economic or other activity on the environment. The term was introduced by the International Association for Impact Assessment in the 1970s in the USA (*Starostina, 2013*). Later, the EIA procedure was adopted in the decision-making system of other countries (Canada, Great Britain, Germany, France, etc.). In Russia, the official beginning of the EIA is considered to be in the 1980s, when the State Committee introduced a requirement to provide information on the results of the planned activities on the environment (*Danilova, 2015*).

Currently, the EIA procedure is mandatory and it is part of the environmental assessment system, both within the Russian Federation and abroad, but its implementation approaches in different countries have a number of distinctive features (*Danilova, 2015*). In Russia, this assessment for all types of planned activities is provided by the Federal law "On Ecological Expertise" (*Federal Law ...*).

Ecological footprint is a method (often defined as an indicator of sustainable development), which allows the level of environmental pressure of anthropogenic activity to be determined at the scale of an individual, a certain group of people, an enterprise, a populated point, a country and even the population of the whole planet (*Mustafayev, 2015*). The idea of creating this method (1992) belongs to the Canadian scientist William Rees, author of the book "Our Ecological Footprint: Reducing Human Impact on the Earth". Nowadays the method is very widespread (*Perminova et al., 2016*).

The "ecological footprint" is based on measuring the consumption by the population of various types of resources (food, materials) in the equivalent of the sea area and biologically productive land, needed for the production of consumed resources and the processing of generated waste. Measurement of energy consumption is simultaneously carried out in the equivalent of area, necessary for absorption of the corresponding carbon dioxide emissions (*Bakumenko, 2008*). As studies show, the current level of consumption of resources by mankind is much greater than the Earth's potential, i.e. the ability of nature to recover, and the ecological footprint of the Earth's population has more than tripled since the 1960s (*Bakumenko, 2008*).

It should be noted that to date, a significant amount of work has been done on calculating the ecological footprint (*Santamouris et al., 2007; Bagliani et al., 2008; Denholm, 2008; Siche et al., 2008; Hoekstra, 2009; Hong et al., 2009, etc.*). Interest in this method is also shown by Russian researchers (*Mozgovaya, 2007; Mozgovaya, 2008; Kulyasov, 2014; Ecological footprint ..., 2014; Mustafayev, 2015*).

A fairly complete picture of the sources and amounts of pollutant emissions in the environment is provided by **Material Flow Analysis**, based on quantitative information

about the input (water, raw materials, energy) and output flows of the system (emissions, wastes). This method can be applied at the level of a single enterprise, or cities, regions, countries, etc. (*Perminova et al., 2016*). The founder of this method is the American scientist of Russian origin V.V. Leontiev, who first applied it in the framework of economic analysis. However, as we see from modern studies, the method has found wide application in assessing environmental status. Based on the equations of material balance, this method allows us to evaluate the effect of industrial enterprises on the environment: to predict and visually display the potential volumes of emissions, discharges, wastes, etc. (*Filkin et al., 2012*). According to *GOST R ISO 14051-2014* (in Russia), Material Flow Analysis is a management tool that can be used to better understand the possible environmental consequences associated with the use of materials and energy, and to improve environmental performance.

In contrast to the work of foreign researchers, actively using this method to assess the environmental quality in general (*Bailey et al., 2004; Suh, 2004; Sendra et al., 2007; Matsubae–Yokoyama et al., 2009, etc.*), in Russia there are only limited examples of its use, mainly in the context of waste management problems (*Tagilova, 2006; Filkin et al., 2012; Starostina, 2013*).

Another method, ***Life Cycle Assessment***, is one of the leading management tools of European countries based on a series of ISO standards. Within the framework of this method, an environmental assessment at all stages of the life cycle is possible: extraction of natural resources/raw materials, production of goods, transportation, consumption/use, disposal in the environment, and all possible intermediate stages (*Starostina, 2013*). Thus, the whole set of consecutive and interrelated links in the production chain is analyzed.

The first life cycle assessment study was conducted in the USA in 1969, by the world famous Coca-Cola company to compare different types of packaging materials. However, the term "life cycle assessment" itself was only proposed by the Society for Environmental Toxicology and Chemistry (SETAC) in 1990 (*Starostina, 2012*). In Russia, the method became known with the adoption of international standards in the

late 1990s - GOST R ISO 14040-14043 (*Pritusalava, 2007*). Life cycle assessment includes four stages: I. Definition of goal and scope; II. Inventory analysis - definition of input (water, raw materials, energy) and output (emissions into the environment, waste) flows; III. Environmental impact assessment, carried out at Midpoint and Endpoint stages, each of which includes certain impact categories; IV. Results interpretation.

It should be noted that this method is the one most frequently used in the framework of modern environmental studies (*Perminova et al., 2016*). At the moment, it is more widespread in the works of foreign researchers. However Russian scientists have also shown considerable interest in this approach, as shown in the following studies (*Sergienko, 2011; Starostina, 2012; Omelchenko, 2013; Eliseeva, 2014; Masleeva, 2014, Yalaltdinova, 2015, etc.*).

A new direction which is becoming more and more important in environmental studies today is ***environmental risk assessment***, which is an interdisciplinary scientific approach that unites specialists of various fields: economics, biology, chemistry and many others (*Gnedaya et al., 2007*). The development of environmental risk assessment first began in the USA in the second half of the 20th century. In 1980, the world's largest international risk analysis society was created, the Society for Risk Analysis, and in 1986 the US Environmental Protection Agency (EPA) developed a series of documents on the procedure for conducting risk assessments. In Russia, work in this area began in the early 1980s, but received serious attention only after the Chernobyl accident (*Shmal, 2010*). The legal basis for applying risk assessment in the Russian Federation is stipulated in the Decree of 10.11.97 "On the Use of Risk Assessment Methodology for the Management of Environmental Quality and Public Health in the Russian Federation."

The main purpose of this assessment is to evaluate the extent and nature of the influence of natural and anthropogenic factors on the environment and living organisms, including human health. In environmental risk assessment, there are two approaches: the ecosystem and sanitary (*Khabarova, 2016*). The former deals with

risks to the natural ecological systems in the unity of their biotic and abiotic components. The second considers the adverse effects on human health.

Environmental risk assessment is based on the identification and prediction of the likelihood of adverse effects, associated with habitat factors. Thus, it allows qualitative and quantitative assessment of risk levels for public health (*Dosmagambetova et al., 2014*), and also proposes measures to reduce risks in environmentally stressed areas (*Gnedaya et al., 2007*).

It should be noted that the methodology of environmental risk assessment is actively used by researchers in many countries (*Wcisło et al., 2002; Gammon et al., 2005; Jiang et al., 2005; Cunningham et al., 2009; McKenzie et al., 2012, etc.*), and is widespread in Russia (*Ivanova et al., 2006; Jankovic et al., 2011; Musikhina, 2012; Osipova et al., 2013, etc.*) for the solution of environmental problems and the management of ecological situation in general (*Priputina, 2012*).

A relatively new approach to environmental assessment uses methods of mathematical modeling of ecological systems or ecological modelling, widely used within environmental risk assessment and in the other contexts such as analysis of regularities of functioning of ecological communities, prediction of ecosystem dynamics (*Abakumov, 2006; Rogovaya, 2007; Zavalishin, 2009; Kondratieva et al., 2013*). Intensively developed in recent years, models are now able to predict global climate change, such as the model IMAGE - Integrated Model to Assess the Greenhouse Effect (*Kahramanova, 2012*).

Due to the fact that environmental modeling, as a scientific approach, is used for a wide variety of purposes, there is no single classification of ecological models. According to *Abakumov (2006)*, three classes of models are distinguished: 1. Descriptive; 2. Qualitative (aimed at studying dynamic features and capable of reproducing dynamic effects in the behavior of the entire system); 3. Simulation models of complex systems (to predict the behavior of systems). It is noted that the latter represent the greatest practical importance (*Abakumov, 2006*). According to another classification (*Kakhramanov, 2012*), there are statistical (for example, the

universal model for estimating soil loss - USLE, as well as WEPP, etc.) and dynamic ecosystems.

In addition, there are several environmental models aimed at studying the anthropogenic impacts on environmental quality, as well as human health (*Rosenbaum et al., 2008*). For example, *the CalTOX model*, which studies the adverse effects on humans, living or working in areas with high levels of contamination, based on a study of the concentration of chemicals in soil, water, air, bottom sediments or plants (*Caltox, 2017*).

The USEtox model, created by the Society for Environmental Toxicology and Chemistry (SETAC) deserves special attention. It should be noted that the team who authored the model consists of research scientists who previously participated in the development and creation of several earlier ecological models, thus, the USEtox model takes into account all the advantages and disadvantages of already existing models. The idea of its creation arose in the early 2000s, but the first version of the model (USEtox version 1.0) became officially available only in 2010 (*Westh et al., 2015*). The USEtox model is an ecological model aimed at characterizing the human and ecotoxicological impacts of chemicals and unites the principles of two methods: Life Cycle Analysis and Risk Assessment (*USEtox, 2017*).

The database of the USEtox model includes information on more than 3000 organic compounds and 25 inorganic metal elements, taking into account their carcinogenic and non-carcinogenic effects, by inhalation and oral penetration. This model can be applied to household indoor air, industrial indoor air, urban air; to sea and fresh water; to natural and agricultural soils. It can also be used in the study of some food products: cereals (rice and wheat), potatoes, tomatoes, lettuce and apples.

One of the advantages of the model is the consideration of the multifactorial effects of chemicals: their intake with air and food is taken into account. Another serious advantage, that represents the uniqueness of the model and the relevance of its use in the context of environmental studies, is the consideration of specific climatic and geographic features of the territory. The world is divided into 8 continental and 17

subcontinental zones, each of which is characterized by different climatic, hydrological, geographic-economic and other parameters. It is worth noting that currently this is the only model known to us, which allows geographical differentiation to be taken into account.

At present, this model is practically unknown in Russia and has not yet found wide application in environmental studies. Perhaps the only example of its use in the Russian Federation is the work of A.R. *Yalaltdinova* (2015), implemented in the framework of a double PhD thesis. However, the model is widely used in the works of foreign researchers (*Querini et al., 2011, Suciu et al., 2012; Marchand et al., 2013; Igos et al., 2014; Morales-Moraet al., 2014; Adam et al., 2015*). It worth noting that the model is recognized and recommended by the world scientific community: the United Nations Environment Program (UNEP), the Society for Environmental Toxicology and Chemistry (SETAC), the European Commission, the Environment and Sustainable Development Institute, the US Environmental Protection Agency (EPA), etc. as the best scientific model for characterizing the toxic effects of chemicals on ecosystems and human health (*Rosenbaum et al., 2008, 2011; Henderson et al., 2011; Westh et al., 2015*).

Brief conclusion

Thus, the presented review demonstrates that at present there are a large number of different methods, approaches, concepts and models for assessing the state of the environment, many of which are also oriented towards the definition and prediction of possible negative effects on living organisms, including human health. Of course, this review does not cover all existing means of environmental assessment, but considered those most often used in modern environmental studies. There is no one unique way of evaluation, each of them is characterized by specific features, and the choice of this or that method depends, first of all, on the goals and objectives of the study. As can be concluded from the present review, one of the specific features of modern means of environmental assessment is the creation of new approaches/methods at the junctions

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of related science fields. In our opinion, the joint use of several methods/approaches/concepts or models can provide more comprehensive assessment of the environmental impact.

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CHAPTER 4. RESEARCH MATERIALS AND METHODS

4.1 Original materials, sampling methods and preparation

To study the peculiarities of bromine accumulation and distribution in the environment, we conducted a comprehensive study, involving sampling of numerous environmental objects. Sampling was mainly carried out in the territory of the Tomsk region. To carry out a comparative analysis, sampling was also done in other regions of the Russian Federation and abroad. When performing the study, the general methodological principles of carrying out ecological and geochemical studies (*Ecological and geochemical features ...*, 2006) were applied. The main research objects, selected and/or prepared by the author in the period from 2011 to 2014, are presented in Table 4.1. Additional material, used in the work and summarized by the author, is listed in Table 4.2. The total number of samples collected and/or prepared by the author is 266.

Table 4.1 - Main objects and research methods

Research objects	Number of samples	Sampling place	Analysis
Soils	20	Tomsk region	INAA, X-ray fluorescence, ICP–MS
	6	France, Grand-Est region	ICP–MS
Drinking water	5	Tomsk region	
	3	France, Grand-Est region	
Salt deposits (scale) of drinking water	38	Tomsk region	
Children's hair	72		INAA, ICP–MS
Blood	30		INAA
Microorganisms of mineral springs	3		
	18		
Poplar leaves (<i>Populus nigra</i>)	10	Tomsk region	
	3	France, Grand-Est region	

Continuation of Table 4.1

Meadowsweet (<i>Filipendula ulmaria</i> (L.) <i>Maxim.</i>)	11	Tomsk region	INAA
Cowberry (<i>Vaccinium vitis-idaea</i>)	5		
Cranberry (<i>Vaccinium oxycoccos</i> L. (1753))	3		
Blueberry (<i>Vaccinium myrtillus</i>)	5		
Food products	34		

Table 4.2 - Research objects, summarized by the author

Research objects	Number of samples	Sampling place	Analysis	Organizations and specialists, who provided materials
Soils	382	Tomsk region, Chelyabinsk region, R. Buryatia	INAA	GEGH TPU, <i>Zhornyak</i> (2009)
Coals	19	Tomsk region		Prof. S.I. Arbuzov, GEGH TPU
Bottom sediments	36			A.U. Ivanov, GEGH TPU
Salt deposits (scale) of drinking water	279	Tomsk region, Samara region, Tyumen region, France, Chelyabinsk region, Pavlodar, Crimea		GEGH TPU
Children's hair	767	Tomsk region, Chelyabinsk region, R. Khakassia, R. Tuva, R. Altai, R. Belorussia, Vietnam, R. Kazakhstan, Irkutsk region	INAA, ICP-MS	GEGH TPU
Blood	325	Tomsk region, Chelyabinsk region, Irkutsk region, R. Kazakhstan	INAA	GEGH TPU; Siberian State Medical University; Ilinskikh N.N., Ilinskikh E.N., Matkovskaya T.V., hospitals of Tomsky and Zyryansky districts; Sukhikh Y.I., Popov V.Y., workers of medical institutions in villages of Tomsk region

Continuation of Table 4.2

Thyroid gland (pathologically altered tissues)	117	Tomsk region	INAA	Denisova O.A., Siberian State Medical University
Biopsy material of human organs and tissues (<i>Homo sapiens Linnaeus 1758 (Primates, Mammalia)</i>)	77			Fedorov S.U., morgue of Tomsky district; Stankevich S.S.
Children's urine	64	Krasnodar region		Alekseenko V.A., USFU
Human milk				Stankevich S.S., Siberian State Medical University
Organs and tissues of pigs (<i>Sus scrofa domestica Linnaeus 1758 (Artiodactyla, Mammalia)</i>)	78	Tomsk region	INAA, SEM	GEGH TPU
Frog (<i>Rana arvalis</i>)	16			Kuranova V.N., TSU
Trush eggshells (<i>Turdus pilaris</i>)	5			Kuranov B.D., TSU
River fish (<i>Perca fluviatilis, Esox lucius</i>)	10			Vietnam
	2	GEGH TPU		
Duckweed (<i>Lemna minor L.</i>)	8	Tomsk region		GEGH TPU
Poplar leaves (<i>Populus nigra</i>)	79	Tomsk region, Baikal territory, R.Kazakhstan		GEGH TPU, Shaimordanova B.H., Asylbekova G.E., PGPI
Meadowsweet (<i>Filipendula ulmaria (L.) Maxim.</i>)	64	Tomsk region, Novosibirsk region, Krasnoyarsk krai, R. Altai, R. Khakassia	INAA	GEGH TPU
Siberian clematis (<i>Atragene speciosa Weinm.</i>)	11	Tomsk region, R. Khakassia, R. Altay, R. Tyva, Krasnoyarsk krai		Shilova I.V., Institute of pharmacology, Tomsk
Alfredia (<i>Alfredia cernua (L.) Cass.</i>)	10			
Bergenia (<i>Bergenia crassifolia</i>)	1			
Cowberry (<i>Vaccinium vitis-idaea</i>)	5	Tomsk region		GEGH TPU
Cranberry (<i>Vaccinium oxycoccos L. (1753)</i>)	7			

Continuation of Table 4.2

Blueberry (<i>Vaccinium myrtillus</i>)	40	Tomsk region, R. Altai, Kemerovo region	INAA	GEGH TPU
Potato (<i>Solanum tuberosum</i>)	27	Tomsk region		

Soils. Sampling was carried out according to GOSTs (*Instruction ...*, 1983, *Methodical recommendations ...*, 1982; *GOST 17.4.3.01-83*; *GOST 17.4.1.02-83*; *GOST 17.4.4.02-84*), as well as methodological developments of the collective IMGRE. The communities of the Tomsk region where the soil sampling took place are presented in Table 4.3.

Table 4.3 – Soil sampling location of the Tomsk region communities

District	Community	Number of samples
Parabelsky	Vysokiy Yar, Novoseltsevo, Chigara	6
Kolpashevsky	Beloyarovka, Inkino, Maraksa, Tyssino, Yudino	6
Chainsky	Kolomenskiye Grivy, Vargater, Ust'-Bakchar, Podgornoye, Bundyur	16
Molchanovsky	Molchanovo, Narga, Tungusovo	5
Krivosheinsky	Volodino, Krivosheino	2
Shegarsky	Melnikovo	2
Kozhevnikovsky	Kozhevnikovo, Urtam, Novopokrovka	33
Tomsky	Khaldeyevo, Naumovka, Novoarkhangel'sk, districts : Oktyabr'skiy, Leninskiy, Sovetskiy, Kirovskiy	182
Asinovsky	Yagodnoye, Novonikolayevka, Filimonovka, Bol'shedorokhovo	15
Pervomaysky	Komsomol'sk	5
Verkhneketsky	Katayga, Sandzhik, Yagodnoye, Stepanovka, Sayga, Belyy Yar, Taynoye, Klyukvinka	14
Teguldetsky	Tegul'det, Chet', Pokrovskiy Yar, Belyy Yar, Beregayevo, Chernyy Yar, Baygaly	20

Continuation of Table 4.3

Zyriansky	Berlinka, Ilovka, Cherdaty, Zyryanka, Tsyganovo, Semenovka	44
Bakcharsky	Kenga, Porotnikovo, Vysokiy Yar, Novaya Burka, Podol'sk, Plotnikovo, Chumakayevka, Polynyanka, Khutorskoye, Bakchar, Chernyshevka, Krylovka, Kedrovka, Vavilovka, Parbig, Bol'shaya Galka, Bogatyrevka, Panychevo	39

Soil sampling was conducted in the last fortnight of March to early April, using the «envelope» method from the topsoil 0–10 cm (the upper fertile layer). Five subsamples of 0.2 kg were selected from each soil pit, giving a total sample of 1 kg from each place. All samples were packed in thick wrapping paper. Pre-treatment of soil samples included the following steps: drying at room temperature, removal of foreign inclusions (vegetation particles, stones, etc.), grinding and progressive sieving (initial sieve hole diameter was 2.5 mm, followed by 1 mm).

Drinking water and the drinking water dry residue. Sampling of drinking water was carried out in five settlements of the Tomsk region (Samus, Naumovka, Kopylovo, Kuzovlevo, Zonalny) and in France, from water supply network taps. Sampling was carried out in accordance with the requirements (*GOST R 51592-2000*).

The sampling of drinking water scale was carried out in accordance with the procedure, set out in the patent No. 2298212 "Method for determining contamination areas of by uranium" from various types of dishes (enameled and electric kettles, pots, boilers, samovars) in which the water, used for drinking, was repeatedly boiled. At the same time, the following information was recorded: the type of dishes used to boil water, and, if possible, the depth of the aquifer. It became clear that the type of heating device does not affect either the chemical or the mineral composition of the salt deposits (*Mongolina, 2011; Soktoev, 2015*). The sampling scheme in the Tomsk region is shown in Figure 4.1.

all requirements and rules, providing for the use of sterile gloves, needles, syringes, etc. from children and adults, together with their personal data. The blood was then dried to a solid state in a muffle furnace at a temperature of 50-60°C using Petri dishes, ground to powder in an agate mortar and packed by 100 mg in foil for further analysis. Blood sampling done in the Tomsk region is presented in Table 4.4.

Table 4.4 - Places of blood sampling in the Tomsk region

District	Community	Number of samples
Aleksandrovsky	Strezhevoy	5
Kargasoksky	Kargasok	4
Chainsky	Podgornoye	1
Shegarsky	Mel'nikovo, Monastyrka, Pobeda, Novo -Il'inka	6
Kozhevnikovsky	Zaytsevo, Kozhevnikovo	3
Tomsky	Loskutovo, Kornilovo, Samus', Kislovka, Kandinka, Tomsk, Naumovka, Chernaya rechka, Seversk	133
Pervomaysky	Tuyendat, Orekhovo	3
Verkhneketsky	Sayga	3
Zyriansky	Zyryanka, Tsyganovo, Semenovka, Berlinka, Cherdaty, Ilovka	62
Bakcharsky	Porotnikovo, Polynyanka, Chumakayevka, Vavilovka, Khutorskoye, Bogatyrevka, Chernyshevka, Novaya Burka, Bol'shaya Galka, Vysokiy Yar, Kedrovka, Bakchar	35

Vegetation. *Poplar leaves* (*Populus nigra*) were selected only from medium-aged trees (20-30 leaves from the tree), from the lower part of the crown at the level of a raised hand, from the maximum number of branches available (trying to use different directions of branches). Sample preparation included: dust removal, washing the leaves with a small amount of distilled water; drying at room temperature; converting to ash in a muffle furnace at a temperature of 450-500°C, subsequent abrasion to powder in an agate mortar, packaging in aluminum foil (100 mg) for analysis.

Sampling of *meadowsweet* (*Filipendula Ulmaria* (L) Maxim), *cowberry* (*Vaccinium vitis-idaea*), *cranberry* (*Vaccinium oxycoccos* L. (1753), *blueberry* (*Vaccinium myrtillus*), microorganism of mineral sources was carried out in summer during the flowering/ early fruiting period. Sample preparation of meadowsweet and microorganisms was carried out in a similar manner: material, dried at room temperature, was crushed and sieved through a sieve with a diameter of 1-3 mm; other types of vegetation were converted to ash in a muffle furnace at a temperature of 450-500°C Prepared samples were packed in aluminum foil for subsequent analysis.

Food products. The analyzed food products: sugar, buckwheat, rice, tea, pasta, bread, milk, coffee, fruit (apples, orange, banana), vegetables (onions, carrots, beets, cucumbers), tomatoes, chicken were bought by the author in November 2015 at the wholesale market of Tomsk. It is worth noting that food products from this market are also delivered to other communities of the region. Solid products that did not need preliminary drying (sugar, buckwheat, etc.) were ground in an agate mortar to a powdery state and packed in foil. The remaining products were dried in a muffle furnace at a temperature of 50-60°C, then crushed and also packaged in foil. Fruits like apples, orange and banana as well as cucumbers and tomatoes were analyzed together. For each food product, three measurements were taken, the results in the work are presented as an average.

4.2 Analytical laboratory research methods

The following methods were used to quantify bromine in environmental components: Instrumental Neutron Activation Analysis (INAA), Inductively Coupled Plasma Mass Spectrometry (ICP-MS), X-ray fluorescence analysis (XRF), and Scanning Electron Microscopy (SEM). All selected materials were analyzed in accredited laboratories using certified methods and standard reference samples. Reliability of analyzes was confirmed by control determinations on different media, internal control was performed.

4.2.1 Instrumental Neutron Activation Analysis

INAA is a modern nuclear-physical method of analysis, characterized by high sensitivity and allowing the content of 28 chemical elements to be determined without taking into account the chemical form of the sample. It is based on the analysis of radioactive isotopes, formed in the sample under the influence of thermal neutron irradiation, and is widely used for samples certification. Its main advantage is the quantitative determination of a significant range of chemical elements from one (even a small - 100-400 mg) sample without destroying it (*Ecological and geochemical features ...*, 2006).

The samples were analyzed using the IRT-T research nuclear reactor in the nuclear-geochemical laboratory (NGL) of the Department of Geocology and Geochemistry of the National Research Tomsk Polytechnic University (accreditation certificate No. POCC RU.0001.518623 dated 10.10.2011, analysts – A.F. Sudyko and L.F. Bogutskaya) according to the instructions of the NSAM VIMS No. 410-YF. The density of the thermal neutron flux in the irradiation channel was $2 \cdot 10^{13}$ neutrons/(cm^2), the duration of irradiation of the samples was 20 hours. The measurements were carried out on a gamma spectrometer with a germanium-lithium detector DGDK-63A. The studies were carried out using a standard reference sample - standard "Canadian elodea" (Figure 4.3).

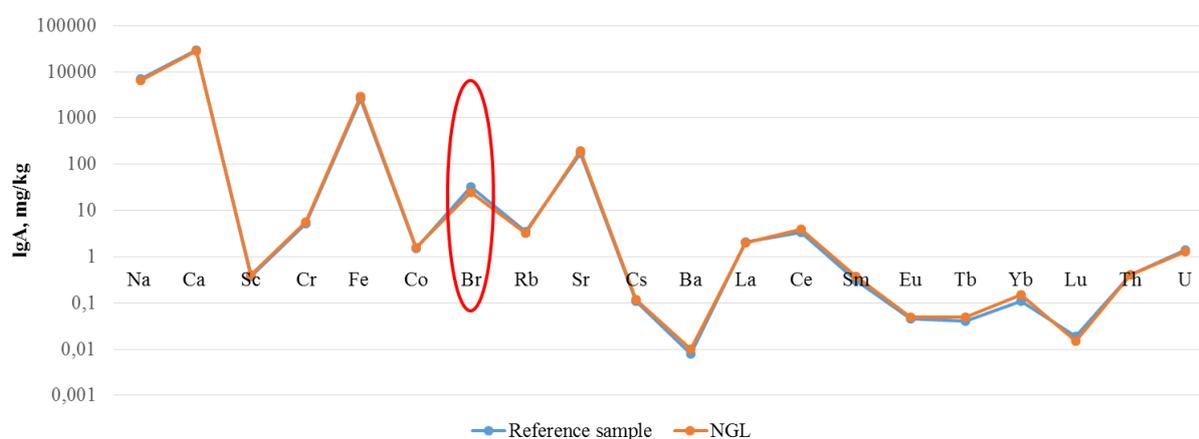


Figure 4.3 - Comparison of the INAA results

The lower limit of bromine detection in natural media (soil, vegetation, solid snow sediment, etc.) by INAA is 0.3 mg/kg (*Ecological and geochemical features ...*, 2006).

4.2.2 Inductively coupled plasma mass spectrometry

ICP-MS is a modern method for determining the elements in small ($\mu\text{g}/\text{kg}$) and ultra-small (ng/kg and less) concentrations. It is based on the use of an inductively coupled plasma as a source of ions and a mass spectrometer for their separation and detection, and allows practically all chemical elements in one sample to be determined in a minimum period of time (about 1 min.).

The samples were analyzed in the analytical center of “Chemical-Analytical Center «Plasma» (Tomsk, accreditation certificate No. ROSS.RU.0001.516895 dated March 25, 2014, director – N.V. Fedyunina). The results of the internal control (each sample was analyzed 3 times) allow us to indicate satisfactory convergence in the majority of the determined chemical elements, including bromine (Figure 4.4).



Figure 4.4 - Internal Control of ICP-MS

4.2.3 X-ray fluorescence analysis

XRF is a modern analytical method allowing us to conduct multi-element analysis, it is characterized by high spectral selectivity to the elements determined. The method is characterized by high expressiveness and relatively simple sample

preparation. The analysis of 20 soil samples was carried out in the testing laboratory of the Institute of Soil Science and Agrochemistry of the RAS Siberian branch, Novosibirsk (Accreditation Certificate No.RA.RU.21AI55 dated July 18, 2016, laboratory leader is A.I. Syso).

4.2.4. Scanning electron microscopy

Electron-microscopic studies were carried out on the basis of the educational and scientific laboratory of electron-optical diagnostics of the "Uranium Geology" at the Department of GEGH TPU, the analyst is S.S. Ilyonok. The main advantages of the SEM method are high resolving power, due to which it is possible to see mineral particles up to tens of nanometers in size, and to conduct quantitative X-ray spectral analysis using an energy dispersive spectrometer (EDS). The material composition of the ash (first of all, the presence/absence of chlorine) of the tubular bone of a domestic pig was studied. The study was carried out on a Hitachi S-3400N scanning electron microscope (resolution 10 nm at an accelerating voltage of 3 kV) with an EDS Bruker XFlash 4010 for X-ray spectral analysis.

4.3 Data processing methods

Processing and generalization of the received analytical material was carried out on a personal computer using Microsoft Office (Excel, Word 2013) and the program "Statistica 7". To build the graphic material, the software "Surfer 10" and "Inkscape 0.91" were used. To create maps of the distribution of bromine in the environmental media, the Kriging method in «Surfer 10» was used. Series were created for the Tomsk region, its separate administrative regions and communities, as well as for the degree of remoteness from the pollution sources.

Data statistical processing (at 95% reliability level) included: average content, standard error, median, mode, minimum and maximum contents, standard deviation, sample variance, variation coefficient. When calculating the average contents of elements from the general series, "hurricane samples" were removed, but they are shown in the scatter of the partial values. As the content of some elements in concentrations below the detection limit of analysis, half of the threshold value was

used in the calculation (*Mikhailchuk, 2006*). The normal distribution of the elements in the sample was checked by Kolmogorov-Smirnov and Chi-square tests.

Regardless of the nature of the bromine distribution, we used the arithmetic mean values for the series as average content levels, which, for both normal and asymmetrical distributions, give the most consistent estimate of the concentration values (*Tkachev, 1975*).

To characterize correlations between bromine content and other chemical elements, Pearson's correlation coefficients for normal distribution and Spearman, when the difference of the distribution was different from normal, were calculated. At the same time, the significance of the correlation was estimated, using a probability counter at the significance level $p = 0.05$ for a given sample size (*Mikhailchuk, 2006*). In addition, according to the results of the cluster analysis, the dendrograms of the correlation matrix were constructed (hierarchical analysis type, distance calculation method - Pearson correlation coefficient). To compare the significance of the differences between the two samples, the Student's test or the Mann-Whitney U test was used, the differences were taken to be significant at the p-level from 0.001 to 0.01.

The following indicators were calculated:

1. *Concentration coefficient*, that is an indicator of anomalous content levels of elements and is calculated as the ratio of the element content in the natural medium (C) to its Clark or background value (C_b)

$$K_k = C/C_b \quad (4.1)$$

For the Clark values the noosphere indicators were used (*Glazovsky, 1982*). To provide background values, depending on the sample series, either the levels of accumulation of elements in specific environmental objects were used, selected from sites remote from urban areas, or the average values for the region. According to the calculated values of the concentration coefficient (for $K_K > 1$), geochemical series were compiled in order of decreasing values.

2. *The total pollution index* (according to *Saet et al., 1990*), which characterizes pollution by several pollutants, was calculated exclusively for soils according to

formula 4.2. As background values for the soils, the data on the reserve forest “Tomsky” was used (Yazikov, 2010).

$$Z_{tpi} = \sum K_k - (n-1) \quad (4.2)$$

where:

K_k is the concentration coefficient,

N is the number of elements studied

According to the value of the total pollution index, there is an indicative scale for assessing pollution levels (Saet et al., 1990), using these indications the following intervals and corresponding pollution levels are allocated:

- less than 16 - low,
- 16 - 32 - medium (moderately hazardous),
- 32 - 128 - high (dangerous),
- over 128 - very high (extremely dangerous).

4.4 Methodology for characterizing human and ecotoxicological impacts of bromine, using the USEtox model

The general mathematical basis of the USEtox model, which is developed in Microsoft Excel, is presented to the fullest extent in the official documents available on the official site (<http://www.usetox.org/>). We have reviewed the basic principles, used to calculate the toxicity impact score of chemicals, bromine in our case.

1. *Toxicity impact score (for human toxicity and freshwater toxicity):*

$$IS = CF_i \times m_i \quad (4.3)$$

with

IS as toxicity impact score (for human toxicity: disability-adjusted life years (DALY); for freshwater ecotoxicity: potentially disappeared fraction (PAF) of species integrated over exposed water volume and time, PAF m³ d),

CF_i as a characterization factor for the potential toxicity impacts of bromine released to compartment i (for toxicity-related impacts on human health: DALY/kg_{Br emitted}; for ecotoxicity-related impacts on ecosystem quality: PDF m³ d/kg_{Br emitted}),

m_i as chemical mass emitted into the compartment i (kg_{Br emitted}/d).

2. *Characterization factors are derived from four factors:*

$$CF_i = FF_i \times XF_i \times EF \times DF \quad (4.4)$$

Fate factor, quantifying the element's dispersal in the environment and representing residence time in a compartment for an emission to a compartment - FF_i ($\text{kg}_{\text{Br in soil}}$ per $\text{kg}_{\text{Br emitted/d}}$);

Exposure factor, quantifying human and/or ecological system contact with environmental media - XF_i (for human exposure: $\text{kg}_{\text{Br intake/d}}$ per $\text{kg}_{\text{Br in soil}}$; for ecosystem exposure: $\text{kg}_{\text{Br bioavailable/kg}_{\text{Br in soil}}}$);

Effect factor - EF (for human toxicity effects: $\text{disease cases/kg}_{\text{Br intake}}$; for freshwater ecotoxicity effects: $\text{PDF m}^3/\text{kg}_{\text{Br bioavailable}}$),

Severity factor - DF , translating impacts into damage (for human health damage: DALY/disease case ; for ecosystem quality damage: PDF/PAF with PAF as the potentially affected fraction of exposed species).

For chemicals causing human toxicity the fate factor and exposure factor can be combined to reflect the intake fraction (iF) for a chemical:

$$iF = FF \times XF \quad (4.5)$$

The iF represents the fraction of the quantity emitted that enters the human population. Intake through inhalation and ingestion is commonly considered in iF calculations.

The human-toxicological effect factor (EF) reflects the change in life-time disease probability due to change in life-time intake of a pollutant ($\text{cases/kg}_{\text{intake}}$). The human-toxicological effect factor is calculated under the assumption of linearity in concentration–response up to the point at which the life time disease probability is 0.5. The human-toxicological effect factor, based on the ED50 results and related to inhalation or oral exposure ($\text{kg/person/lifetime}$), is calculated by:

$$ED50_{ing} = \frac{ED50_{a,t} \times BW \times LT \times N}{AF_a \times AF_t \times 10^6} \quad (4.6)$$

$$ED50_{inh} = \frac{ED50_{a,t} \times INH \times LT \times N}{AF_a \times AF_t \times 10^6} \quad (4.7),$$

with

$ED50_{a,t}$ is the daily dose for animal a (e.g. rat) and time duration t (e.g. subchronic) per kg body weight that causes a disease probability of 50% for corresponding exposure route ($\text{mg}\cdot\text{kg}^{-1}\cdot\text{day}^{-1}$),

AFa the extrapolation factor for interspecies differences,

$A Ft$ is the extrapolation factor for differences in time of exposure, i.e. a factor of 2 for subchronic to chronic exposure and a factor of 5 for subacute to chronic exposure,

BW is the average body weight of humans (70 kg),

INH is the average human inhalation rate ($13 \text{ m}^3\cdot\text{day}^{-1}$),

LT is the average lifetime of humans (70 years),

N is the number of days per year ($365 \text{ days}/\text{year}^{-1}$).

The ecotoxicological effect factor is calculated by determining the linear slope along the concentration–response relationship up to the point where the fraction of affected species is 0.5. The ecotoxicological effect factor of a chemical equals:

$$\log\text{HC50} = \frac{1}{n_s} * \sum_s \log EC_{50_s} \quad (4.8)$$

where $EC50$ data is the water concentration at which 50% of a population displays an effect (e.g. mortality). Aquatic ecotoxicological effect factors have the dimension m^3/kg ,

n_s is the number of species.

3. To be compatible with the characterization of bromine emissions, measured bromine concentrations in soil had to be converted into an estimate of emitted mass to soil, assuming that concentrations in soil are at steady-state:

$$m_i = C_i \times V_{\text{soil}} \times \rho_{\text{soil}} \quad (4.9)$$

where

m_i ($\text{kg}_{\text{Br emitted}}$) is estimated continuous bromine mass emitted to soil, back-calculated from the measured bromine concentration in soil identified by INAA,

C_i is concentration, measured in $\text{mg}_{\text{Br in soil}}/\text{kg}_{\text{soil}}$ and multiplied by 10^{-6} to arrive at $\text{kg}_{\text{Br in soil}}/\text{kg}_{\text{soil}}$,

V_{soil} (m^3_{soil}) is the bulk soil volume in a considered region,
and ρ_{soil} ($\text{kg}_{\text{soil}}/\text{m}^3_{\text{soil}}$) is the bulk soil density.

Brief conclusion

Thus, the work is based on material samples, the selection and preparation of which were carried out in accordance with normative documents and certified procedures. Modern highly sensitive analytical methods of research, along with the use of modern software and traditional methods of statistical data processing, make it possible to consider the results obtained as reliable with a high degree of accuracy.

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**CHAPTER 5. BRIEF NATURAL CLIMATIC AND
GEOECOLOGICAL CHARACTERISTICS OF THE
TOMSK REGION**

The Tomsk region is a region of the Russian Federation situated in the south-eastern part of the West Siberian plain - the largest plain in the world. The area of the Tomsk region is 316.9 km², which is larger than most European countries. It borders with Krasnoyarsk Krai in the east, Tyumen and Omsk oblasts in the west, and Novosibirsk and Kemerovo oblasts in the south (*Evseeva, 2001*). This region includes 16 administrative districts (Figure 5.1). The administrative center is Tomsk city. The region is inhomogeneous with the majority of the population living in the southern part of the Tomsk region near rivers, roads and railroads.

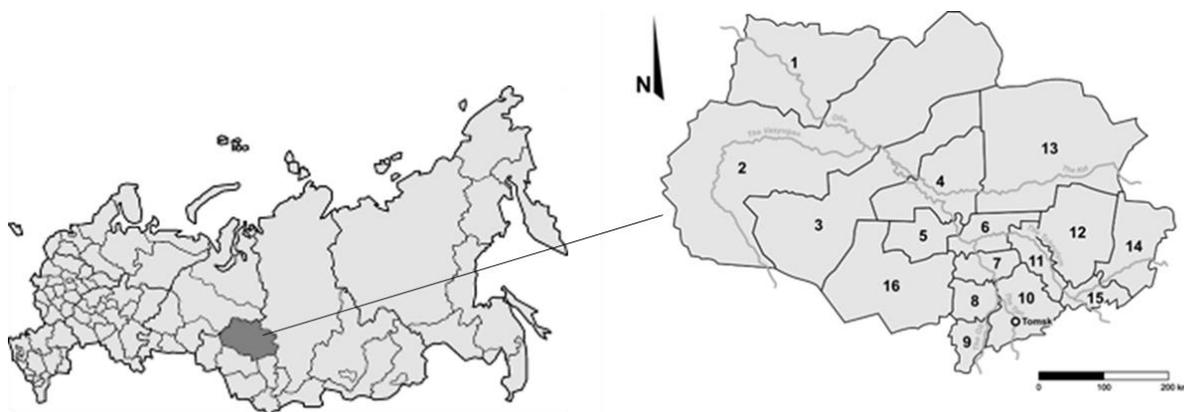


Figure 5.1 - Geographical location of the Tomsk region and its administrative structure

Districts: 1 – Aleksandrovsky, 2 – Kargasoksky, 3 – Parabelsky, 4 – Kolpashevsky, 5 – Chainsky, 6 – Molchanovsky, 7 – Krivosheinsky, 8 – Shegarsky, 9 – Kozhevnikovsky, 10 – Tomsky, 11 – Asinovsky, 12 – Pervomaysky, 13 – Verkhneketsky, 14 – Teguldetsky, 15 – Zyryansky, 16 – Bakcharsky.

The climate of the Tomsk region is transitional: from temperate to sharply continental. It is characterized by short, warm summers, long, cold winters, late spring and early autumn frosts. The level surface and openness of the region's territory from the north and south favor the free penetration of air masses from the Arctic and Central Asia. This is one of the causes of weather instability. The average annual air temperature is negative and varies from -0.6°C in the south to -3.5°C in the northeast. The annual precipitation amount varies on average from 400 to 570 mm, with the

greatest loss falling in the west, as well as in the east and northeast, while approaching to the Central Siberian highland (*Evseeva, 2001*).

More than 97% of the territory of the Tomsk region belongs to the West Siberian Plain. Within the territory of the region, we can distinguish the Ketsko-Tymskaya, the Chulym, the Priarginskaya, the East-Barabinsky and the Vasyuganskaya inclined plains. In the central part of the region, within the valley of the Ob river, the Ob-Tymskaya lowland stretches from the south-east to north-west (*Evseeva, 2001*).

The relief of the Tomsk region, which is flat and swampy, favors the accumulation of bromine, precisely because of the presence of a significant number of bogs in the region (average percentage of marshland is 39.5-50% (*Dyukarev, 1991*). According to *Selivanov, 1939* the bogs are particular bromine biogeochemical provinces. In general, across the relief of the region, a number of hypsometric levels can be distinguished: the Ob River divides the region into a relatively elevated (up to 193 m) right-bank part and a lower left bank. The most elevated is the Tom'-Yai interfluve, where the spurs of the Kuznetsk Ala-Tau come in. The highest point of the Tomsk region (264 m) is located here, from which the land descends in a north-west direction. The minimum height is 30 m and is confined to the Ob river at the northern boundary of the region (*Evseeva, 2001*).

Soil-forming rocks, which according to *G.A. Konarbaeva (2004, 2008)* do not play a serious role in the accumulation of bromine at present, but were capable of serving as the source of the element in the process of their formation, have alluvial, lacustrine-alluvial, lacustrine, and water-glacial genesis within the region. The soil-forming process on the territory of the region is characterized by a number of distinctive features: close dependence on the properties of the parent substrate; stratification of deposits; increased water cut in the northern and central part of the region; strong influence of meso- and microrelief on soil formation; carbonate depletion of soil-forming rocks within the middle taiga and enrichment in the southern; climate severity; prolonged freezing and slow snow defrosting, contributing to waterlogging; close relationships of distribution of plant communities with lithology

of rocks and soil climate. All these factors are dependant on the location of the site, which determines the type of soil formed : sod, podzol and swamp. This means that the soil cover of the region is diverse. The main morphological and chemical properties (thickness of the humus horizon, structure, mechanical and chemical composition, severity of soil-forming process) are distinguished by automorphic, semi-hydromorphic and hydromorphic soil types.

As for the geological structure, the territory of the Tomsk region is located in the southeast of the Western-Siberian epipaleozoic slab, which contains a foundation with loose Mesozoic-Cainozoic cover. The former consists of the lower-folded floor, composed of metamorphosed rocks of the Precambrian and Paleozoic and the upper is represented by a complex of deposits of the Paleozoic and Lower Mesozoic (*Zemtsov, 1988*). The thickness of the loose sedimentary rocks of the Mesozoic-Cenozoic cover varies from several meters to 5.5 km in depressions.

Tomsk region's geological and hydrogeological structure is extremely important in the study of bromine, since bromine is a typical halogen, i.e. salt forming element, formed in the sedimentation conditions. For this reason, in salt deposits and brines it acts as a geochemical indicator of their genesis (*Bromine in salt deposits..., 1976*). As the analysis of data on halogen regions of the world shows, the scale of salt accumulation in different geological epochs is characterized by sharp differences. In ancient times, salt accumulation was often much more intense. The most significant was the Permian salt accumulation. Significant amounts of salts were deposited in the Cambrian, Devonian, Triassic, Jurassic, Cretaceous and Miocene times (*Yanshin, 1985*). It should be noted that some of the deposits of the above-mentioned periods are also found in the territory of the Tomsk region (Figure 5.2). It is rather difficult to confirm the genesis of these sediments. According to the majority of researchers, the deposits of these periods indicate their marine genesis, while other authors tend to the version of salt transfer from the continent, considering their genesis as continental. Individual researchers also associate the removal and deposition of salts with volcanism and thermal waters (*Yanshin, 1985*). However, almost all researchers adhere

to the hypothesis of an endogenous salt source. It is believed that endogenous deep brines were transported from the upper mantle to the sedimentation basins in which they quickly concentrated, due to deep heating, and, upon cooling, they deposited salts (*Yanshin, 1985*).

From the point of view of the tectonic structure, the Western Siberian Plate is distinguished by an outer belt, to which the southern part of the Tomsk region belongs, and by an inner (central) region, within which structures of isometric shape are developed - shafts, arches, anticlines, depressions (*Evseeva, 2001*). The foundation of the plate was formed by tectonic movements of two types: associated with the postmodern inherited development of the structural and formational zones of the geosynclinal stage, and with the formation of large faults during the stretching of the crust in the Early Mesozoic. Movements of the first type were manifested in the linear distribution of positive and negative forms of the basement relief. Deep grabens were created by the movements of the second type (*Zemtsov, 1988*).

Most of the Tomsk region is located in the southeast of the West Siberian artesian basin, with some reaching into the central part, characterized by waters of different composition: up to a depth of 500 m, they are hydrocarbonate-calcium and, at deeper levels, hydrocarbonate-sodium (*Shvartsev, 1998*). According to hydrogeochemical data (Fig. 5.3), a regional sub-meridional zone is distinguished in the Ob-Yenisei interfluvium extending up to the Yenisei river, which is transitional in chemical composition between the Cretaceous buried mineralized sea chloride waters on the left bank of the Ob river, and hydrocarbonate infiltration waters of the right-bank (*Ermashova, 1982; Nazarov, 2004*).

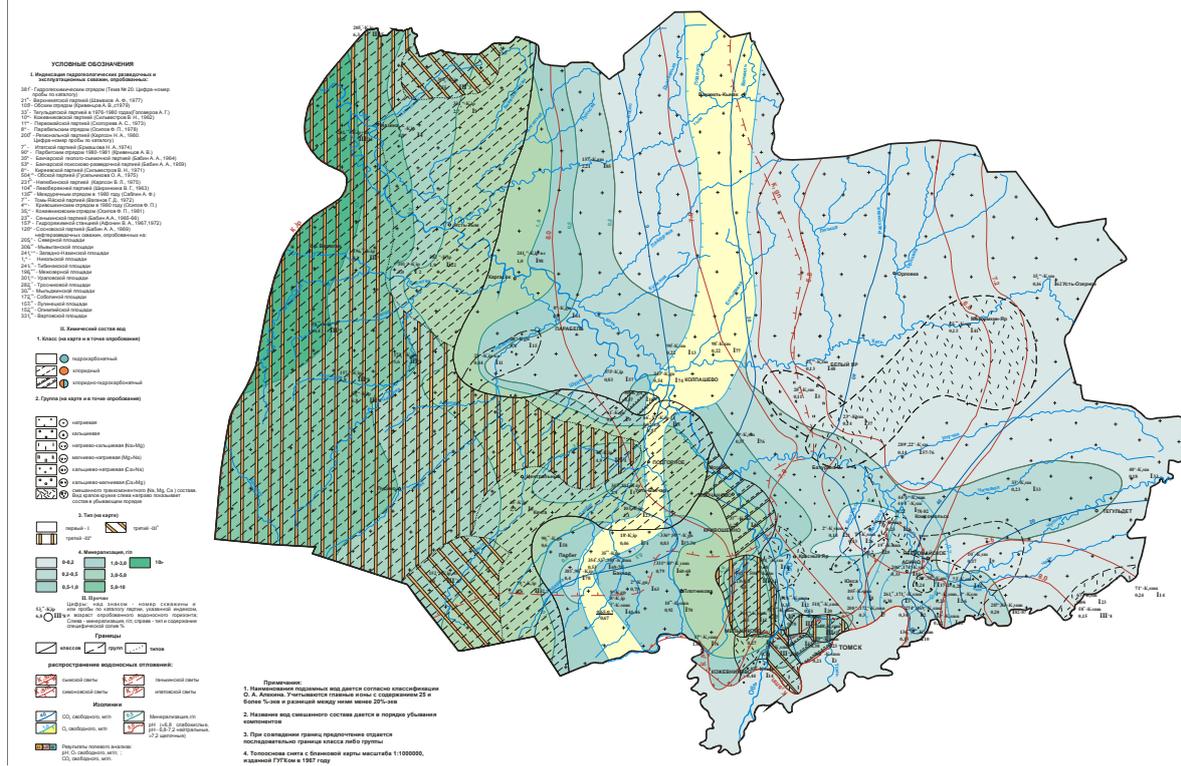


Figure 5.3 - Hydrogeochemical map of the territory of the Tomsk region
(Ermashova, 1982)

The region’s fresh water zone is confined mainly to rocks of the upper Paleogene, Neogene and Quaternary, while the capacity of the zone of these waters is a unique formation, associated with the continuation of the continental sedimentation conditions throughout the entire Mesozoic and Cenozoic. The zone of saline waters is represented by hydrocarbonate chloride and chloride-sodium waters, formed in sea basins of low salinity. The zone of brines is found in the western, central and northern parts of the Tomsk region and is confined to the rocks of the Jurassic and Paleozoic basement. The Tomsk region is rich in balneological waters, including bromine and iodine-bromine, slightly less in bromine-siliceous (Evseeva, 2001).

At the same time, the Tomsk region has a wide range of natural resources potentially rich in bromine, primarily combustible minerals. Deposits of brown coal are found in the territory of the region, divided into Neogene, Jurassic and Late Paleozoic age groups, and located mainly in the southeastern part of the Ob-Irtysh coal basin (Rare elements in coals, 2007). About 18% of Russia's peat reserves are located

in the Tomsk region, where over 1,300 peat deposits have been identified. Over 100 hydrocarbon deposits have been discovered in the region, the main oil and gas bearing districts are Aleksandrovsky, Kargasoksky and Parabelsky. There are also deposits of mineral ores: the Bakcharskiy iron ore deposit field (*Nikolaeva, 1967, Pshenichkin, 2011*), zircon-ilmenite placers (*Rikhvanov et al., 2001*), bauxite, zinc, gold, etc. (*Evseeva, 2001*). They are also of interest in the study of bromine, since the element can occur in the form of rare bromides in the oxidation zones of some ore deposits.

In addition to the wide variety of natural factors and conditions of the Tomsk region, which can significantly influence the accumulation of bromine, potential anthropogenic sources of the element's entry into the environment are also observed in its territory. They are spread over the whole territory of the region and are connected, first of all, to the exploitation of the various mineral deposits. The release of bromine into atmospheric air can also be associated with the use of biomass, coals, gas, etc., used for heating purposes. Particular attention should also be paid to the areas where detachable parts of launch vehicles fall during launches from the Baikonur cosmodrome (Figure 5.4), which leads to their contamination with rocket fuel products since bromine (bromine pentafluoride) is widely used as a propellant oxidant (*Yoffe et al., 2013*).

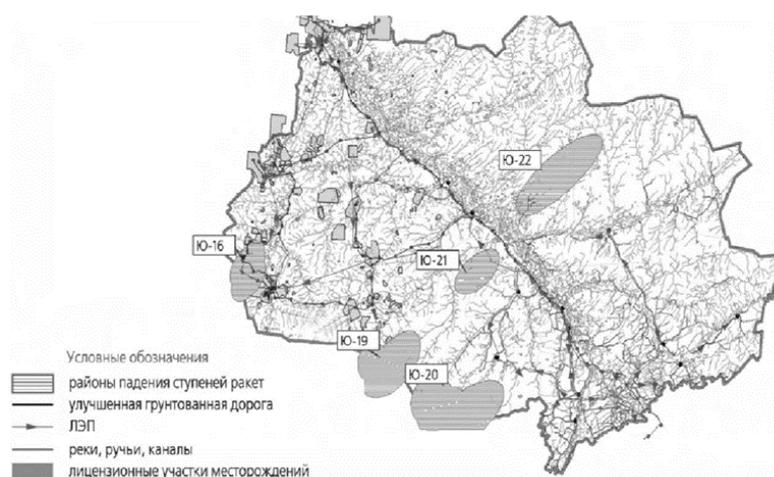


Figure 5.4 - Areas where the detached parts of launch vehicles in the Tomsk region may land (*Environmental monitoring..., 2012*).

However, among all the districts of the region, Tomsky district is of particular interest (Figure 5.5). Attention has been already drawn to it for several decades (*Ecology of the Northern ...*, 1994; Rikhvanov, 1997; Shatilov, 2001; Baranovskaya, 2003; *Ecological and geochemical features ...*, 2006; Yazikov, 2006; Talovskaya, 2008; Zhornyak, 2009; Rosenbaum, 2011, Mongolina, 2011, Baranovskaya, 2011, Filimonenko, 2015, etc.) in view of the complex ecological situation that has arisen here due to the presence in a relatively limited area of a significant number of industrial enterprises (the Northern Industrial Zone) (*Ecology of the Northern ...*, 1994). Within this zone, there are over thirty different production complexes, among which there are also potential bromine sources: the world's largest nuclear fuel cycle enterprise - the Siberian Chemical Combine, and the largest oil and gas processing plant in Russia. Other possible sources of bromine in the Tomsk region include several other companies in the following sectors: petrochemical and chemical, pharmaceutical and heat.



Figure 5.5 - Scheme of location of major industrial complexes on the Tomsky district territory (Yazikov, 2006)

Note: 1 - industrial enterprises: 1) Tomsk Petrochemical Combine; 2) thermal electric power station; 3) greenhouse complex; 4) treatment facilities of Tomsk Petrochemical Combine; 5) ash-disposal area of thermal electric power station; 6) industrial waste landfill; 8) cattle farm; 9) base of the "Himstroy" administration; 10) gas transmission base of the gas pipeline; 11) the base of agropromstroy; 12) Mezheninovskaya poultry farm; 13) «Tomsky» state farm; 14) poultry farm manure storehouse; 15) city dump; 16) pig complex pond-store; 17) Tugan poultry farm; 18) coal storage; 19) pig complex sewage farm; 20) "TIZ"; 21) "Roltom"; 22) "Sibkabel"; 23) «Shpalozavod»; 24 "Drozhhzavod"; 25) GRES-2; 26 ABZ ("Ashot") (production of building materials); 27) ship-repair shore base; 28) Sausage making shop "Rybolovsky"; 29) ABZ; 2 - sites of liquid radioactive waste; 3 - production wells of water supply intake; 4 - communication lines; 5 - pipeline; 6 - power lines; 7 - highways; 8 - railway; 9 - borders of medical districts.

Brief conclusion

Thus, the set of natural and anthropogenic conditions of the territory of the Tomsk region is characterized by great heterogeneity, which contributes to the formation of various geochemical conditions and factors that determine the peculiarities of accumulation, distribution, and patterns of migration of bromine in the environment, and determines the complexity of its entry pathways.

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**CHAPTER 6. PECULIARITIES OF BROMINE
ACCUMULATION AND DISTRIBUTION IN THE
ENVIRONMENTAL COMPARTMENTS OF THE TOMSK
REGION**

On the basis of the available material, we analyzed the accumulation and distribution of bromine in the biotic and abiotic components of the biogeocoenoses of the Tomsk region (Figure 6.1). The data presented makes it possible to carry out a clear differentiation in bromine concentration levels in various research objects.

It can be clearly seen that the bromine content in coals, soils, drinking water and bottom sediments of the region does not exceed 20 mg/kg (mg/l for drinking water) with a relatively low variation coefficient: for all objects it is no more than 50%, and only for soils - 79%. It is worth paying special attention to these research objects, since they are one of the first links in the biogeochemical migration of chemical elements. The second group includes the drinking water scale and a solid sediment of snow, the average content of which does not exceed 20 mg/kg, but the values of the variation coefficients are in the range of 200 to 250%.

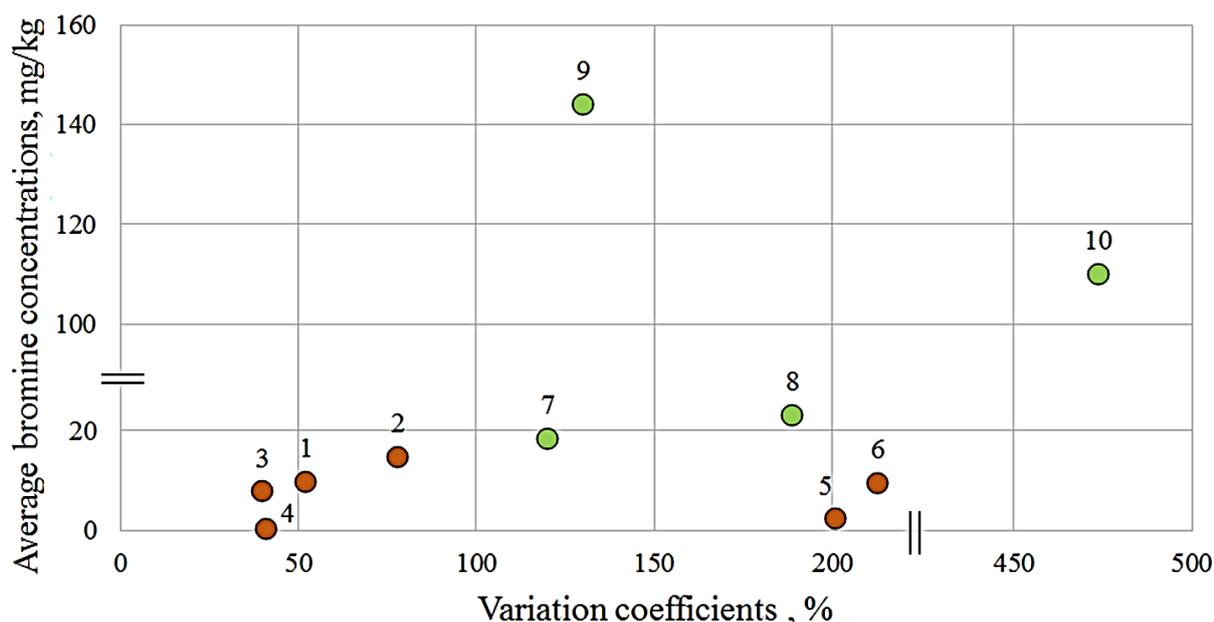


Figure 6.1 - Levels of bromine accumulation (average content) in the abiotic and biotic components of the environment of the Tomsk region, mg/kg

Note: 1 - coals, 2 - soils, 3 - bottom sediments, 4 - drinking water (mg/l), 5 - scale of drinking water, 6 - solid snow sediment (data for the West Siberian region, according to Shatilov, 2001), 7 - microorganisms of mineral sources, 8 - plant organisms, 9 - animal organisms, 10 - human body; in brown - abiotic components, in green - biotic.

Unlike the biogenic and biogenic substances, where we see the geochemical homogeneity of Br accumulation, complex living organisms show a completely different picture. Chaotic geochemical accumulation of the halogen is clearly reflected in concentration ranges from 18.3 mg/kg in microorganisms to 144 mg/kg in terrestrial animals, with a difference of the variation coefficient from 120 to 474%, the maximum variability being in children's hair. This indicates, first of all, that living organisms are able to concentrate enough high amounts of the element and can be effective indicators of the changes taking place in nature, under the influence of natural factors and anthropogenic activity.

6.1 Features of accumulation and distribution of bromine in abiotic components

A detailed description of the levels of bromine accumulation in the abiotic components of the environment of the Tomsk region is presented in Figure 6.2.

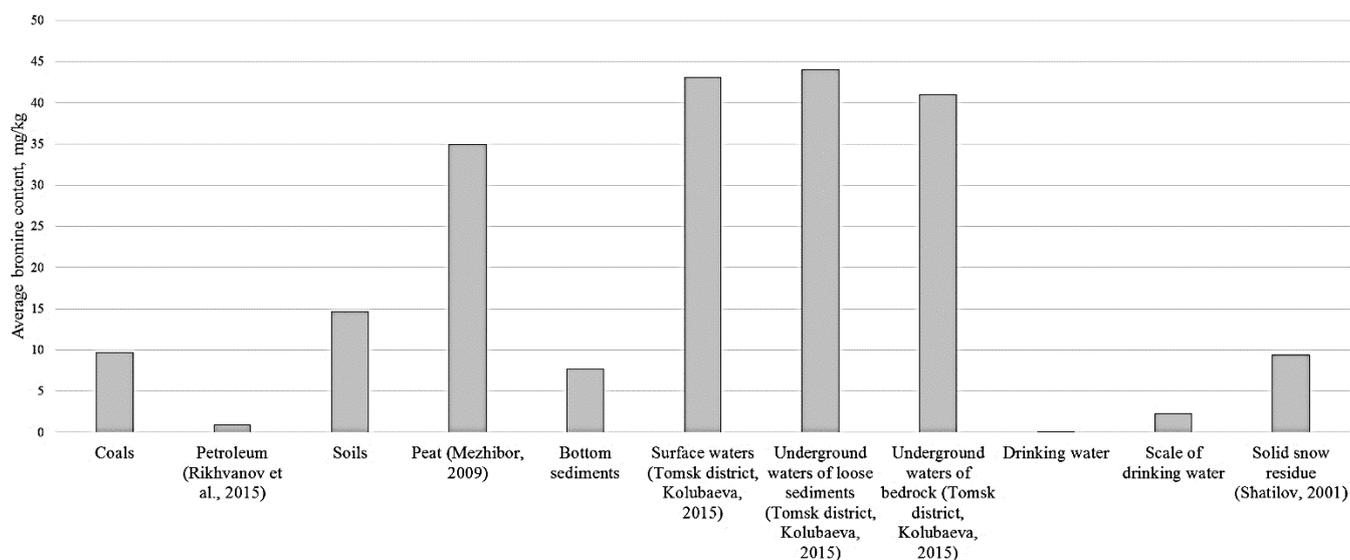


Figure 6.2 - Average bromine content in abiotic environmental components, mg/kg (mg/l in water)

The content of bromine in the coals of the Tomsk region exceed the Clark content (Yudovich, 2006). However, the content of the element is less than in Belgium and Kuzbass coals as well coals of Bulgaria and Ukraine (see Table 2.4). The concentrations of bromine in the petroleum of the Tomsk region is quite low, in

Chapter 6. Peculiarities of bromine accumulation and distribution in the environmental compartments of the Tomsk region comparison to the literature data. We do not undertake to judge this fact in the framework of this work.

Soils

Analysis of statistical parameters (Table 6.1) along with the spatial distribution of bromine in the soils of the Tomsk region (Figure 6.3) show that the lowest content of the halogen is observed in the soils of Tomsky district, the highest in the soils of Kozhevnikovsky and Bakcharsky districts. It should be noted that in the latter one, elevated levels of the element accumulation in soils are observed in all settlements we studied (*Perminova et al., 2017; Shaikhiev, 2017*).

Table 6.1 - Statistical parameters of the distribution of bromine in the soils of the Tomsk region, mg/kg

District	N	X	λ	Min	Max	Mo	Me	V,%
Parabelsky	6	14,8	1,7	9,0	22,1	–	14,5	29
Kolpashevsky	6	11,9	2,1	7,5	21,3	–	10,4	43
Chainsky	16	15,3	2,0	5,0	31,8	5,0	13,1	54
Molchanovsky	5	14,5	1,1	11,1	18,0	–	14,4	17
Krivosheinsky	2	16,8	3,8	13,0	20,1	–	16,8	32
Shegarsky	2	14,3	1,3	13,0	15,6	–	14,3	13
Kozhevnikovsky	33	29,8	1,5	0,5	35,8	–	18,8	47
Tomsky	182	9,1	0,4	0,5	59,5	0,5	8,9	65
Asinovsky	15	19,7	1,8	5,0	31,8	23,4	20,8	35
Pervomaysky	5	15,6	3,2	5,0	23,9	14,4	14,4	46
Verkhneketsky	14	13,6	2,2	4,4	30,1	–	10,7	60
Teguldetsky	20	13,2	1,4	5,0	28,0	5,0	12,4	48
Zyriansky	44	10,8	1,0	3,9	34,4	6,1	8,6	62
Bakcharsky	39	40,3	1,9	15,2	64,9	–	41,3	29
<i>Tomsk region</i>	<i>389</i>	<i>14,5</i>	<i>0,6</i>	<i>0,5</i>	<i>64,9</i>	<i>0,5</i>	<i>11,1</i>	<i>79</i>

Note: N - number of samples; X - average value; λ - standard error; Min and Max - minimum and maximum values, respectively, Mo - mode, Me - median, V - variation coefficient.

Chapter 6. Peculiarities of bromine accumulation and distribution in the environmental compartments of the Tomsk region

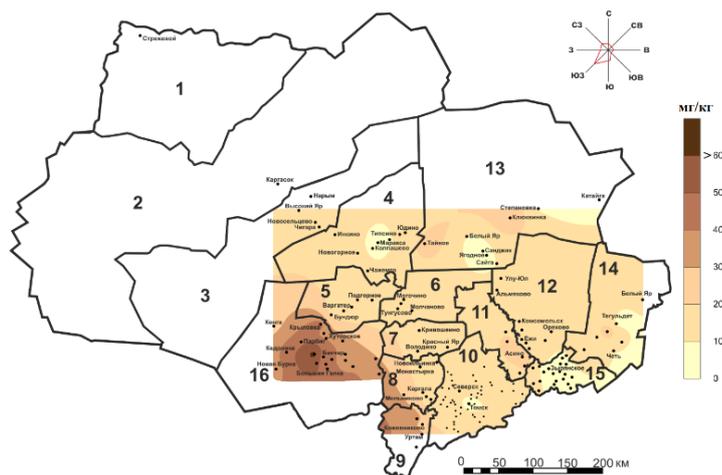


Figure 6.3 - Schematic map of the distribution of bromine (mg/kg) in the soils of the Tomsk region

Note (districts): 1 – Aleksandrovsky, 2 – Kargasoksky, 3 – Parabelsky, 4 – Kolpashevsky, 5 – Chainsky, 6 – Molchanovsky, 7 – Krivosheinsky, 8 – Shegarsky, 9 – Kozhevnikovsky, 10 – Tomsky, 11 – Asinovsky, 12 – Pervomaysky, 13 – Verkhneketsky, 14 – Teguldetsky, 15 – Zyriansky, 16 – Bakcharsky.

We can also judge the bromine enrichment of the soils of the Tomsk region, relative to the background values of the reserve forest "Tomsky", on the basis of the calculated concentration coefficients of chemical elements, (Yazikov, 2006). Values of bromine concentration coefficients exceed 10 units for soils in almost all districts of the region, and bromine contribution to the total pollution index (TPI) varies from 12.6 to 43.6 % (Table 6.2).

Table 6.2 - The concentrations coefficients of chemical elements and the contribution of bromine in the total soils pollution index of the districts of the Tomsk region

District	Concentrations coefficient			Br contribution (%) to TPI
	1-5	5-10	>10	
Parabelsky	(Ba,Tb) _{4,8} Ta _{4,4} Ca _{4,3} U _{3,8} Au _{3,3} Rb _{2,9} Sb _{2,6} Cs _{2,3} (Yb,Hf) _{2,1} Na _{1,9} (Cr,Lu) _{1,8} Co _{1,7} (Fe,Th) _{1,5} Ce _{1,3} (La,Sr,Sm) _{1,2}	Ag _{8,0}	Br_{12,3}	24,2%
Kolpashevsky	Tb _{4,4} Sb _{4,2} Ta _{4,1} Ca _{4,0} U _{3,9} Rb _{3,2} Na _{2,7} Hf _{2,6} Cr _{2,4} (Lu,Au) _{2,3} Yb _{2,1} Cs _{1,7} (Fe,Co,Sr) _{1,6} Th _{1,5} (Ce,Sm) _{1,4} La _{1,2}	Br_{9,9} Ag _{8,0} Ba _{5,8}		19,1%
Chainsky	Ba _{4,9} Sb _{4,4} Ag _{4,0} Lu _{3,8} Yb _{3,7} Cs _{2,9} Co _{2,4}	Ta _{8,3} Rb _{8,0} Ca _{7,9} Tb _{7,2} U _{6,9} Au _{5,9}	Br_{12,7}	16,5%

Chapter 6. Peculiarities of bromine accumulation and distribution in the environmental compartments of the Tomsk region

	(Na,Fe) _{2,3} (Cr,Th) _{1,9} (Hf,La) _{1,7} Sm _{1,6} Ce _{1,5} Sc _{1,3} Sr _{1,1}			
Molchanovsky	Sb _{4,5} Ag _{4,0} Rb _{3,4} (Cr, Yb) _{3,2} Ca _{3,0} Cs _{2,8} Lu _{2,6} Na _{2,4} (Fe,Co) _{2,1} Th _{1,8} (Ce,Sm) _{1,7} (La,Hf) _{1,6} (Sr,Au) _{1,4} Sc _{1,2}	Tb _{8,9} Ta _{8,9} U _{6,2} Ba _{5,4}	Br_{12,1}	18,8%
Krivosheinsky	(Rb,Ag) _{4,0} Cr _{3,6} U _{3,5} Yb _{3,1} Au _{3,0} Sb _{2,6} Ca _{2,3} Cs _{2,2} (Na,Lu) _{2,1} (Fe,Co) _{1,9} Sm _{1,8} (Ce,Th) _{1,6} Hf _{1,5} La _{1,3} Sc _{1,1}	Ta _{7,7} Tb _{6,5} Ba _{5,8}	Br_{14,0}	24,5%
Shegarsky	Sb _{4,5} Ag _{4,0} Cs _{3,9} Rb _{3,2} Ca _{3,0} Yb _{2,9} Cr _{2,7} Na _{2,4} Lu _{2,3} Fe _{2,2} Co _{2,0} Au _{1,9} Th _{1,7} Ce _{1,6} (La,Hf) _{1,5} Sm _{1,4} Sc _{1,2}	Ta _{7,7} Tb _{7,5} U _{6,3} Ba _{5,5}	Br_{11,9}	19,6%
Kozhevnikovsky	Rb _{4,8} Ca _{3,6} Cs _{3,4} Yb _{3,3} Sb _{3,0} Cr _{2,6} Lu _{2,5} (Fe, Ba) _{2,4} U _{2,3} (Na,Co) _{2,2} Th _{2,1} (As,Ce) _{1,8} (La,Hf) _{1,6} Sc _{1,5} Ag _{1,4} Sm _{1,3}	Tb _{5,5} Ta _{5,3}	Br_{15,1}	29,2%
Tomsky	U _{4,9} (Au,Rb) _{4,7} Ba _{4,4} Ca _{3,7} Yb _{3,0} Cs _{2,9} Cr _{2,6} (Na,Lu) _{2,5} Fe _{2,4} Co _{2,2} Th _{2,0} Hf _{1,8} Ce _{1,7} (Sm,La) _{1,5} Sc _{1,4}	Br_{7,8} Tb _{7,7} Sb _{7,1} Ag _{5,6} Ta _{5,2}		12,6%
Asinovsky	Lu _{4,5} Yb _{3,6} Ba _{3,3} Cs _{2,9} Na _{2,8} (Fe,Co) _{2,1} Ag _{2,0} Th _{1,7} (Cr,La,Sm,Hf) _{1,5} (Sc, As,Ce) _{1,3} Sr _{1,1}	Ca _{8,2} Rb _{7,9} Ta _{7,6} U _{6,6} Au _{6,5} Tb _{5,6} Sb _{5,4}	Br_{16,4}	21,5%
Pervomaysky	Lu _{4,0} Yb _{3,4} Na _{2,6} Sr _{2,5} As _{2,2} (Fe, Co) _{1,5} (La,Hf) _{1,4} (Cs,Sm) _{1,2} Th _{1,1}	Ca _{9,7} Au _{8,0} Rb _{7,4} Ta _{6,6} Tb _{6,5} Sb _{6,3} U _{5,6} Ba _{5,2}	Br_{13,0}	18,0%
Verkhneketsky	Ba _{3,9} Cr _{3,5} Ta _{3,3} Tb _{3,0} Rb _{2,8} U _{2,5} (Na,Ca) 2,0Sb _{1,9} Au _{1,8} (Sr, Yb) _{1,5} (Cs,Lu,Hf) _{1,3}	Ag _{5,3}	Br_{11,3}	33,0%
Teguldetsky	(Sb,Tb) _{4,7} U _{4,6} As _{3,8} Ba _{3,7} Rb _{3,2} (Cs, Yb) _{2,6} (Ag,Lu) _{2,0} Co _{1,9} (Na,Fe) _{1,6} Sr _{1,5} (Hf,Th) _{1,3} (La,Ce,Sm) _{1,2}	Au _{8,1} Ca _{7,6} Ta _{5,8} Cr _{5,2}	Br_{11,0}	18,0%
Zyriansky	Tb _{4,4} Ca _{4,2} Ba _{4,0} (Rb,U) _{3,7} Sb _{3,6} Ta _{3,1} Cr _{3,0} Ag _{2,8} (Yb,Lu) _{2,1} Cs _{1,9} Fe _{1,6} (Na, Co) _{1,4} Th _{1,3} (La,Ce) _{1,2} Hf _{1,1}	Br_{9,0} Au _{5,6}		21,2%
Bakcharsky	Rb _{4,6} U _{4,5} Ag _{4,0} (Sb,Cs) _{3,4} (Ca, Ba) _{3,1} (Co, Yb) _{2,5} Au _{2,4} Lu _{2,3} Cr _{2,2} Th _{2,1} Fe _{2,0} Ce _{1,7} Na _{1,6} La _{1,5} (Sm,Hf) _{1,4} Sc _{1,3} Sr _{1,1}	Ta _{7,3} Tb _{6,0}	Br_{32,9}	43,6%

As comparative analysis shows (Figure 6.4), the element's average content in the soils of the Tomsk region exceeds the values observed in the soils of some other regions of Russia and abroad. The maximum concentration of the halogen, observed in the soils of Bakcharsky district, is much higher than the concentrations of Br in almost all of the

Chapter 6. Peculiarities of bromine accumulation and distribution in the environmental compartments of the Tomsk region soils, with the exception of the UK and Japan, which are characterized by totally different territorial geomorphological and climatic conditions as well as proximity to the sea and the deposition of volcanic material (*Perminova et al., 2017*).

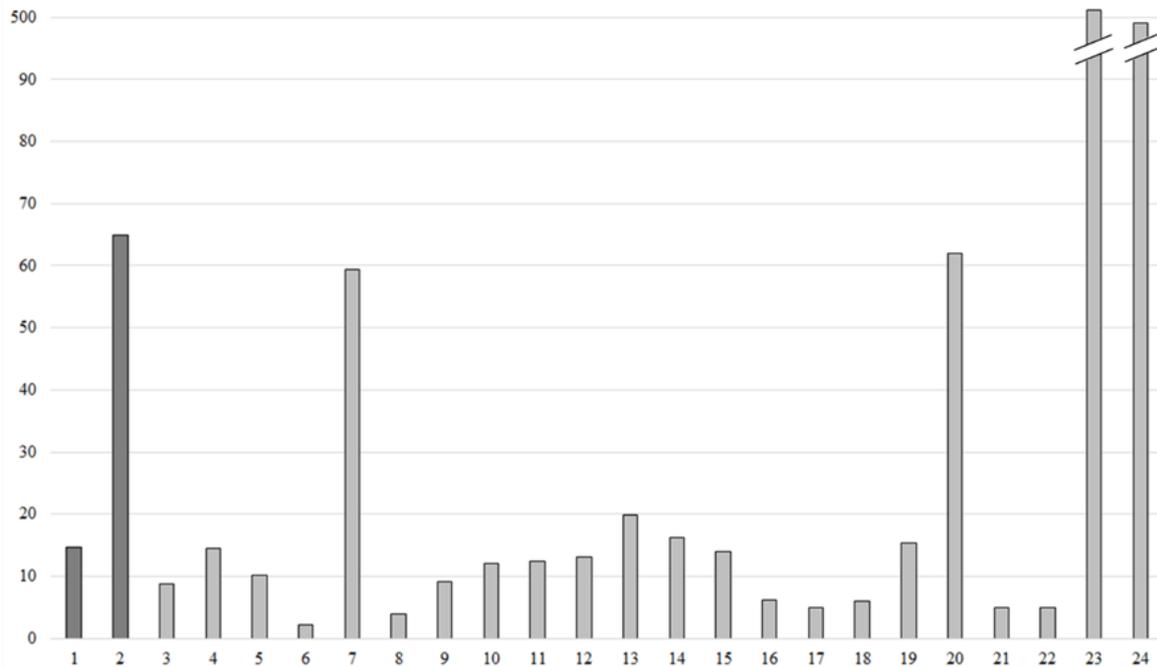


Figure 6.4 – Bromine content in the soils of Russian regions and foreign countries, mg/kg

Note: 1 - Tomsk region (average content), 2 - Tomsk region (maximum content, Bakcharsky district), 3 - Tomsk, 4 - Chelyabinsk, 5 - Pavlodar, 6 - R. Buryatia, 7 - Western Siberia, 8 - Vasyugan plain, 9 - Kulundinskaya plain (chernozem), 10 - Southeastern Transbaikalia, 11 - Baraba plain, 12 - Priobskoe plateau (chernozem), 13 - Pisa, 14 - Livorno, 15 - Norway, 16 - France, 17 - China, 18 - USA, 19 - Jordan (without fumigants), 20 - Jordan (with fumigants), 21 – world soils, 22 - clarke for soils, 23 - Great Britain, 24 - Japan (*Perminova et al., 2017*).

We cannot unequivocally explain the genesis of high concentrations of bromine in the soils of Kozhevnikovskiy and Bakcharsky districts. It is true that Bakcharsky district is located in the southern part of the region, where detachable parts of carrier rockets are discarded during launches from the Baikonur cosmodrome (Figure 5.4).

However, the fact is that increased bromine content is not observed in soils of other areas of the region, which are also areas where the carrier rockets fall.

What we cannot exclude is the impact of natural sources. Some authors note that the entry of bromine to the earth's surface can occur with brines from the earth's interior (including the mantle) along deep faults (*Bakiev, 2006*). In both areas of the region, which are partially located within the Barabinsko – Pikhtovaya megamonolysis, located between the Tomsk and Novosibirsk regions, several deep faults are observed (*Evseeva, 2001, Belkin, 2017, Tectonics of the Tomsk region ... , 2017*). The possible transfer of bromine in hydrothermal solutions is also indicated by *A.G. Mironov and S.M. Zhmodik (1991)*, according to which, it is able to pass into the fluid phase due to its low solubility in the acid melt. It appears that the soils as well as the snow cover (*Sobolev, 2013*) can reflect geochemical anomalies of an endogenous nature.

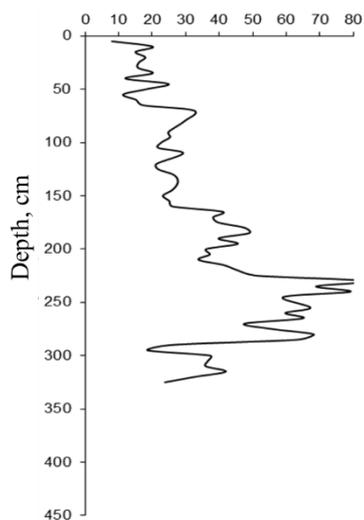
Coefficients of pair correlation in the soils of Kozhevnikovsky and Bakcharky districts (Table 6.3) indicate the association of bromine with other elements (Ba, Sc, TR, U, etc.), accompanying organic matter. Such kinds of association of the elements are characteristic, for example, for the platonogenic deposits of the Bazhenov formation, formed as a result of sedimentation-diagenetic accumulation (*Gavshin, 1984*). Apparently, the association of bromine in the soils of the two districts can be regarded as natural and formed as a result of sedimentation and diagenesis in the marine environment, which once again proves the possible arrival of the element with brines from the earth's interior.

Table 6.3 - Coefficients of pair correlation of bromine with chemical elements in soils and peat of the Tomsk region districts

Elements	Districts								
	Chainsky	Kozhevnikosky	Tomsky	Asinovsky	Verkhneketsky	Teguldetsky	Zyriansky	Bakcharsky	Bakcharsky
	Soils								Peat (Mezhibor, 2009)
Na	0,22	0,27	0,18	0,34	0,78	0,19	0,11	0,37	0,15
Ca	0,55	0,03	0,4	0,33	0,75	0,42	0,53	0,51	0,87
Sc	0,92	0,24	0,4	0,33	0,85	0,01	0,19	0,37	0,07
Cr	0,58	0,29	0,29	0,1	0,21	0,54	0,36	0,33	0,08
Fe	0,2	0,19	0,42	0,75	0,8	0,12	0,17	0,34	0,29
Co	0,13	0,13	0,32	0,54	0,8	0,43	0,16	0,21	0,13
As	0,08	0,22	0,26	–	0,12	–	–	0,23	–
Rb	0,87	0,03	0,37	0,61	0,02	0,19	0,16	0,29	0,13
Sr	–	0,37	0,13	–	0,15	0,18	0,22	0,28	0,53
Ag	–	0,27	0,02	–	0,16	–	0,04	–	0,13
Sb	0,29	0,19	0,07	0,56	0,03	0,08	0,24	0,26	0,06
Cs	0,52	0,11	0,14	0,26	0,64	0,02	0,15	0,21	0,09
Ba	0,28	0,36	0,05	0,19	0,51	0,01	0,02	0,4	0,18
La	0,35	0,3	0,5	0,65	0,86	0,48	0,14	0,49	0,03
Ce	0,13	0,36	0,29	0,65	0,87	0,14	0,05	0,33	0,05
Sm	0,34	0,03	0,55	0,06	0,7	0,43	0,24	0,4	0,02
Eu	0,51	0,24	0,34	0,23	0,54	0,5	0,14	0,23	0,03
Tb	0,72	0,17	0,53	0,25	0,79	0,4	0,13	0,41	0,04
Yb	0,22	0,14	0,34	0,55	0,84	0,51	0,24	0,55	0,02
Lu	0,65	0,22	0,46	0,66	0,91	0,43	0,15	0,39	0,05
Hf	0,22	0,42	0,2	0,61	0,68	0,04	0,02	0,27	0,06
Ta	0,13	0,14	0,09	0,73	0,69	0,01	0,11	0,03	0,10
Au	0,85	0,23	0,4	0,08	0,08	0,04	0,05	0,06	0,42
Th	0,41	0,18	0,37	0,08	0,78	0,14	0,17	0,43	0,07
U	0,64	0,36	0,31	0,6	0,8	0,12	0,14	0,46	0,42

Note: only those districts in which a minimum of 10 samples were selected were considered; the probability level is 95%; negative correlation links are highlighted in red; significant positive links are shown in bold.

It is noteworthy that the researches of A.M. Mezhibor (2009) on the study of bogs



in the Tomsk region showed that the Bakcharskoye bog, located in the Bakcharsky district, is also characterized by the highest bromine contents relative to the peats of the region. The average Br content in it is 35.4 mg/kg of dry matter, accumulated mainly in the lower layers (Figure 6.5), which indicates the natural source of its intake. In addition, identical geochemical associations of bromine with calcium, iron, and uranium are noted in the soils and peats of the Bakcharsky

district (Table 6.3).

Figure 6.5 - Distribution of bromine with depth in the Bakcharsky swamp (Mezhibor, 2009)

Thus, we can conclude that the soils of the Tomsk region are enriched with bromine, and its distribution is fairly homogeneous. The smallest content of the element is noted in the Tomsky district and the highest in the Kozhevnikovskiy and Bakcharsky districts. An analysis of the available literature suggests the possible natural genesis of bromine in the soils of the last two districts due to the arrival of the element in the form of fluids/gas with brines from the earth's interior through deep faults.

Water and drinking water scale

Analysis of Figure 6.2 shows that the highest bromine content is observed in the natural underground and surface waters of the region, which correspond to the background level and are regarded as characteristic of ecologically clean areas (Kolubaeva, 2015). Lower concentrations of the element are characteristic for drinking water.

The actual material on the study of drinking water in 5 settlements of the Tomsk region allows us to conclude that the levels of accumulation of bromine (Br^-) in water are not characterized by anomalous contents of the element and do not exceed the maximum allowable concentrations, established for the bromide ion in drinking water (SanPin 2.1. 4.1116-02). In addition, supplementary drinking water samples, collected

Chapter 6. Peculiarities of bromine accumulation and distribution in the environmental compartments of the Tomsk region in France, demonstrate that the concentrations of the element in drinking water in the settlements of the Tomsk region are lower (Figure 6.6).

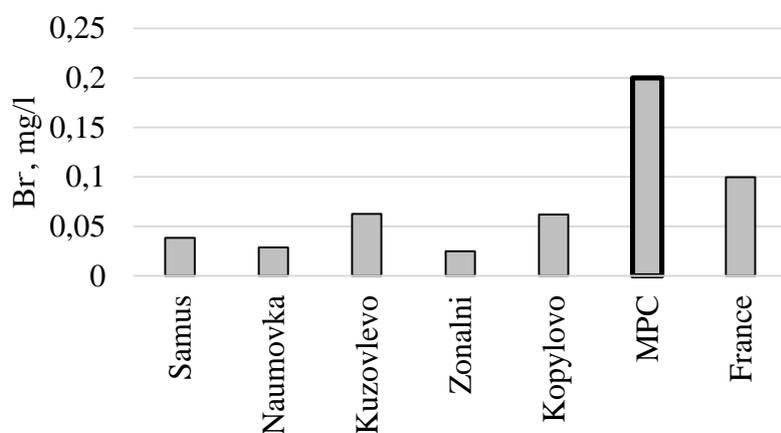


Figure 6.6 - Content of bromine (Br⁻) in drinking water (mg/l) of settlements of the Tomsk region and France, with indication of MPC for drinking water

Accumulation of bromine in the scale of drinking water may be due to evaporation processes, which are widely distributed for bromine in natural environments (A.I. Perel'man, 1972). Water's high boiling point, in combination with some specific physical - chemical properties of bromine, such as its high saturated vapor pressure value - 28700 Pa at 25°C, which determines the volatility of bromine (for comparison: the saturated vapor pressure value for mercury is 0,264 Pa at 25°C), and the fact that bromine is a highly mobile element in the waters of any chemical composition (A.I. Perel'man, 1972), can cause the formation of a geochemical evaporative barrier in a domestic environment, enabling its accumulation in the dry residue. Thus, the analysis of the features of bromine accumulation requires particular caution when studying drinking water scale.

Analysis of the spatial distribution of bromine in the scale of drinking water across the territory of the Tomsk region (Figure 6.7), as well as statistical parameters (Table 6.4) indicate a heterogeneous distribution of the element.

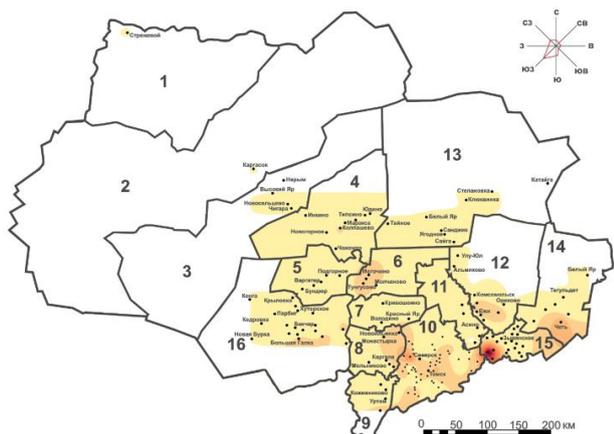


Figure 6.7 - Schematic map of the distribution of bromine (mg/kg) in the scale of drinking water in the Tomsk region

Several anomalous geochemical fields are noted on the territory of the Tomsk region, with one of them extending from Zyryansky to Shegarsky district, largely passing through and covering the Tomsky one. Minimum levels of regional bromine accumulation in the scale of drinking water are observed in the Kargasoksky district, and the highest in Tomsky. Variation coefficients of bromine in the scale of drinking water are less than 100% for such districts as Aleksandrovsky, Chainsky, Molchanovsky, Krivosheinsky, Shegarsky, Kozhevnikovsky and Bakcharsky. In Kolpashevsky, Asinovsky, Pervomaysky, Verkhneketsky and Teguldetskiy districts, the coefficients of variation do not exceed 135%, while in Tomsky and Zyryansky districts they make up 144% and 388% respectively, indicating a highly heterogeneous distribution of the element in the scale of these areas, especially in the latter. Such high variability in its content can be associated with both complex natural conditions of groundwater formation and the impact of anthropogenic activity.

Table 6.4 - Statistical parameters of the distribution of bromine in the scale of drinking water in the districts of the Tomsk region, mg/kg

District	N	X	λ	Min	Max	Mo	Me	V, %
Aleksandrovsky	2	0,9	0,5	0,4	1,4	–	0,9	79
Kargasoksky	2	0,3	–	0,3	0,3	0,3	0,3	–
Parabelsky	6	0,5	–	0,5	0,5	0,5	0,5	–
Kolpashevsky	15	1,4	0,4	0,5	4,6	0,5	0,5	103
Chainsky	8	1,4	0,5	0,3	3,1	0,3	1,1	91
Molchanovsky	7	3,3	0,4	1,5	4,8	–	3,1	34
Krivosheinsky	4	2,3	0,2	1,9	2,8	–	2,3	16
Shegarsky	3	2,4	0,6	1,4	3,3	–	2,5	40

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Kozhevnikovsky	5	2	0,9	0,3	5	0,3	2,1	98
Tomsky	83	3,8	0,6	0,2	47,7	0,5	2,8	144
Asinovsky	7	1,2	0,6	0,3	3,7	0,3	0,3	121
Pervomaysky	12	1,8	0,6	0,3	5,7	0,3	0,8	107
Verkhneketsky	7	0,7	0,3	0,3	2,4	0,5	0,5	101
Teguldetsky	20	1,3	0,3	0,3	8,9	0,3	0,3	134
Zyriansky	88	0,8	0,1	0,1	57,3	0,1	0,7	388
Bakcharsky	37	1,8	0,2	0,1	5,4	0,9	1,2	76
<i>Tomsk region</i>	<i>306</i>	<i>2,3</i>	<i>0,3</i>	<i>0,1</i>	<i>57,3</i>	<i>0,5</i>	<i>1,2</i>	<i>200</i>

Note: *N* - number of samples; *X* - average value; λ - standard error; *Min* and *Max* - minimum and maximum values, respectively, *Mo* - mode, *Me* - median, *V* – variation coefficient.

As the comparative analysis of the levels of bromine accumulation in drinking water scale in the Tomsk region and other regions of Russia and abroad (Figure 6.8) shows, its bromine content in the Tomsk region is one of the lowest, along with the Tyumen region.

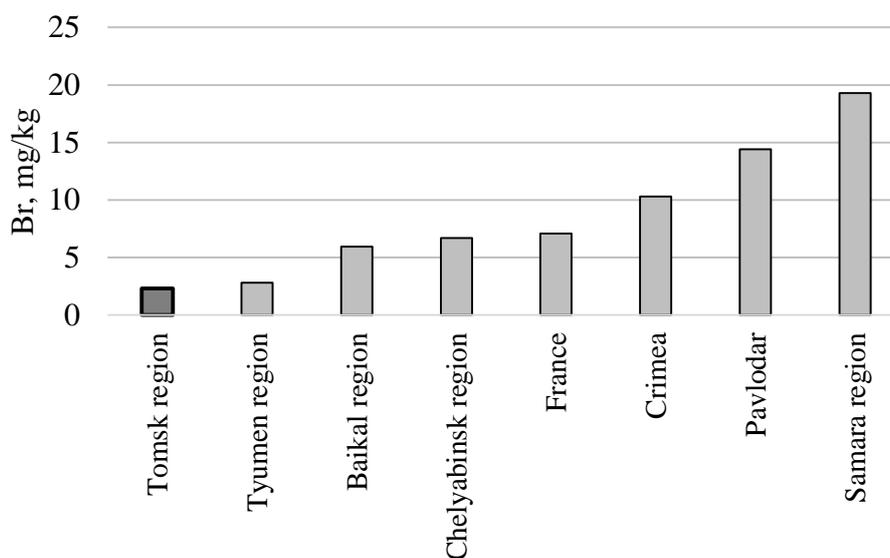


Figure 6.8 – Bromine content in drinking water scale (mg/kg) of the Tomsk region and other regions of Russia and abroad

In our opinion, this is due to the completely different hydrogeological conditions of the territories, while the bordered Tomsk and Tyumen regions, located in the West Siberian plain, have similar hydrogeological complexes (*Geology and minerals...*, 1999).

Thus, bromine in the scale of drinking water should be studied with special care in view of possible evaporation barrier, which takes place in domestic conditions and contributes to the accumulation of the element. Its distribution in the Tomsk region is not homogeneous. The smallest content of the element is observed in the Kargasoksky district, and the highest in the Tomsky district. At the same time, a comparative analysis demonstrates that the content of bromine in the scale of drinking water of the Tomsk region is significantly lower than in other territories of Russia and abroad.

6.2 Features of accumulation and distribution of bromine in biotic components

The analysis of the material (Figure 6.9) shows that the living substance is actively able to concentrate bromine, and the content can vary significantly. It should be noted that multidirectional geochemical reactions, characteristic of living matter and taking place in aerobic and anaerobic environments often with the participation of microorganisms, predetermine the diversity of incompatible occurrence forms of elements (Yaroshevsky, 2004).

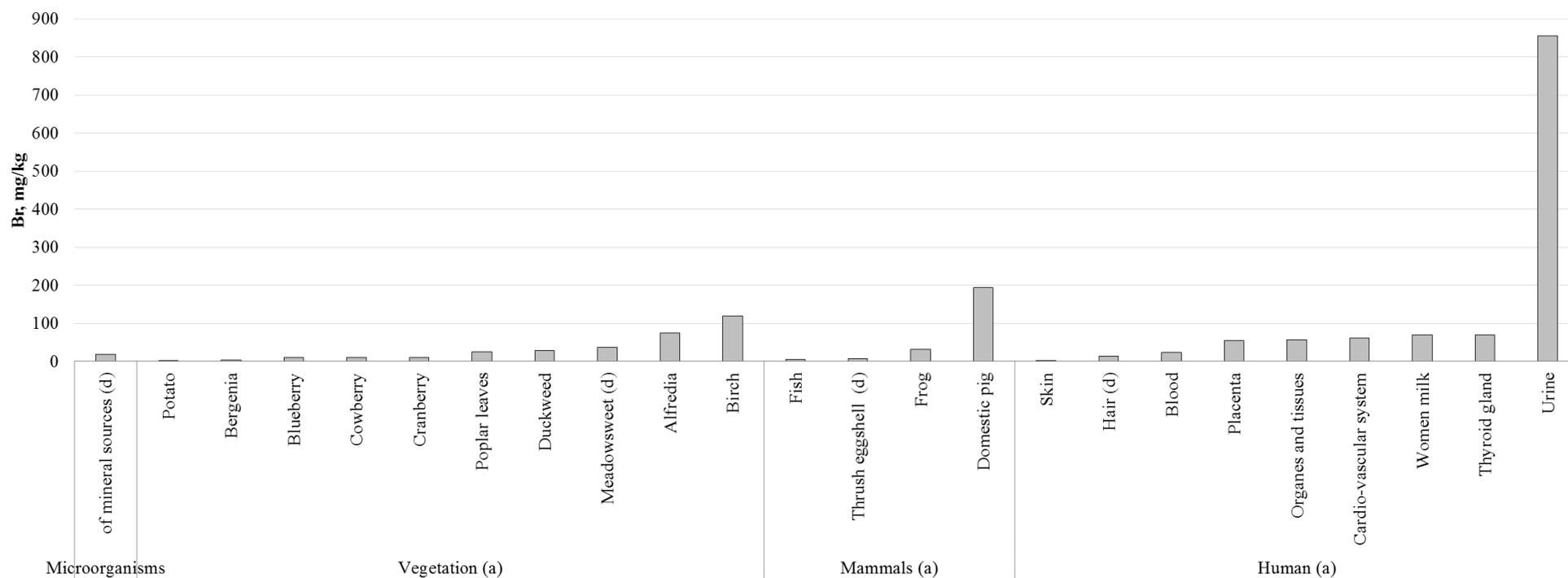


Figure 6.9 - Average bromine content in the living organisms of the Tomsk region (mg/kg of dry matter - d or ash - a)

Microorganisms of mineral springs

Microorganisms of mineral sources (mats) are biocenoses, consisting of prokaryotes and located at the bottom of water bodies or in their coastal zones. In their shape, they are similar to mold films. The mat is a highly integrated community with an extremely complex trophic structure. It consists of producers and consumers of the first order, as well as decomposers that receive organic matter from the upper layers along the detrital chain. Studies show that the mat is one of the most balanced ecosystems: it produces exactly as much organic and oxygen as it spends immediately in the process of its life activity (*Perminova, 2012, 2013*). Based on the results of the comparative analysis, it can be concluded that the levels of bromine accumulation in the mats of the Tomsk region are higher than in the mats of the Baikal region, the average content of the element being 18.3 and 8.5 mg/kg, respectively.

Vegetation

The study of the chemical composition of vegetation has become very widespread, as a fundamental basis for understanding biogeochemical cycles in ecosystems and landscapes. This is due to the fact that plants are one of the most sensitive components, reflecting both air and soil pollution (*Kabata-Pendias, 1989; Kabata-Pendias, 2011*). It is noted, for example, that the leaves of city-center poplars, contain 26-60 times more bromine than leaves from the suburbs (*Harmful chemicals, 1989*). The study of medicinal plants for which L.S. Selivanov noted bromine specificity is particularly relevant. In addition, *N.V. Baranovskaya (2011)* showed that bromine passes from the dry part of the plant to a pharmacologically active extract. The results of a comparative analysis of levels of bromine accumulation in plant species of the Tomsk region and other territories are shown in Figure 6.10.

Chapter 6. Peculiarities of bromine accumulation and distribution in the environmental compartments of the Tomsk region

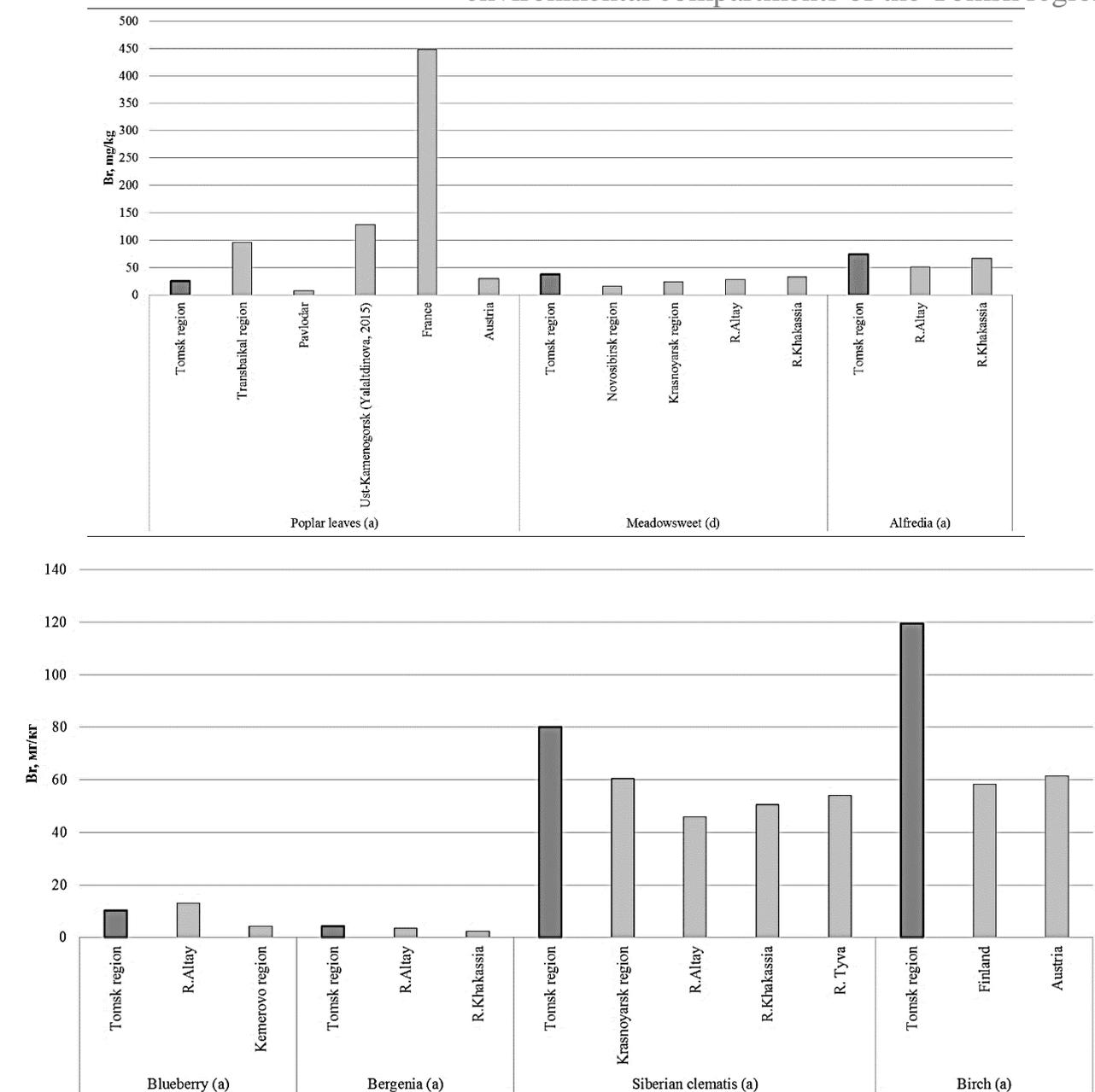


Figure 6.10 - Bromine content in plants of the Tomsk Region and other regions of Russia and abroad (mg/kg of dry matter or ash)

As can be seen, the levels of bromine accumulation in the leaves of black poplar (*Populus nigra L.*) in the Tomsk region are significantly lower than those of practically all the areas under consideration, with the exception of poplar trees in Pavlodar. Abnormally high content of the element is noted in poplar leaves, selected near a petrochemical plant in France. Levels of bromine, concentrating in the meadowsweet, alfredia, blueberry and bergenia of different territories are relatively close. Elevated

levels of the element are also noted in the Siberian clematis and birch tree in the Tomsk region, in comparison with other territories.

Regularities of bromine accumulation and distribution in animal organisms

Animal organisms are no less sensitive to changes occurring in the environment than plants. However, they reflect a more complex intake of elements, since they are a post-plant link in the food chain. Analysis of the content of bromine in the ash of organs and tissues of the domestic pig (Figure 6.11) shows that the concentrations of the element in two organisms, living in different territories, can vary significantly. However, even despite these differences, there are similar trends in the accumulation of the element.

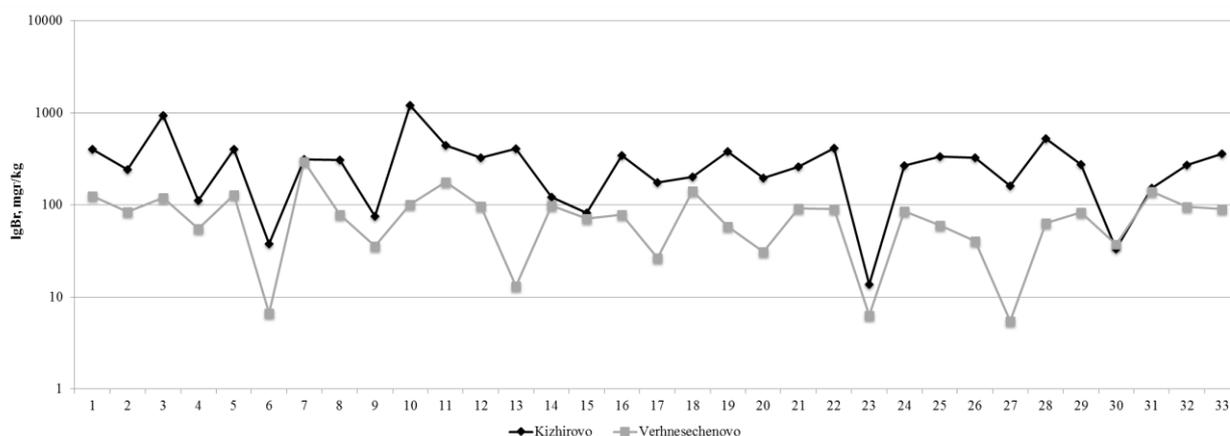


Figure 6.11 - Levels of bromine accumulation in the organs and tissues of domestic pig of (mg/kg) of two settlements of Tomsky district

Note: 1 - bronchus, 2 - inner fat, 3 - eye, 4 - brain, 5 - stomach, 6 - teeth, 7 - skin, 8 - hooves, 9 - blood, 10 - lungs, 11 - uterus, 12 - mammary gland, 13 - bladder, 14 - muscle tissue, 15 - liver, 16 - esophagus, 17 - vertebra, 18 - kidney, 19 - rectum, 20 - ribs, 21 - spleen, 22 - heart, 23 - spinal cord 24 - large intestine, 25 - small intestine, 26 - trachea and Adam's apple, 27 - tubular bone, 28 - ear, 29 - tail, 30 - bristle, 31 - thyroid gland, 32 - tongue, 33 - duodenum

Moreover, the concentration of the halogen in each system of organisms of two piglets also has several differences (Figure 6.12). The maximum concentrations of bromine are noted in the respiratory and sensory systems. It is noticeable that,

regardless of the site of selection of piglets, identical levels of accumulation of the element in the nervous and endocrine systems are noted.

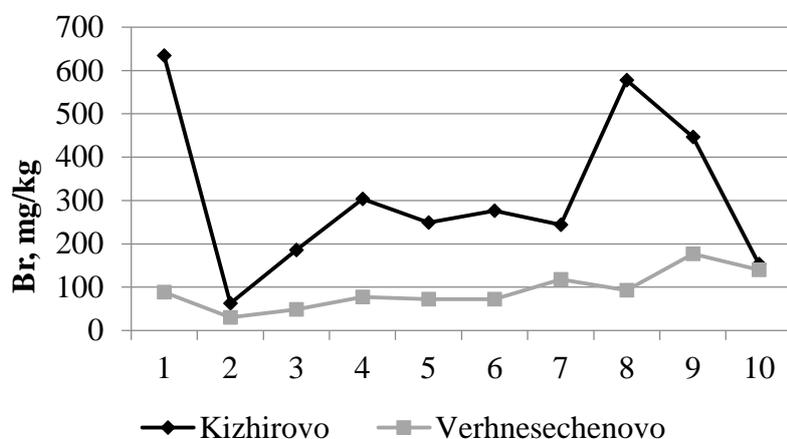


Figure 6.12 - Levels of bromine accumulation in systems of domestic pigs (mg/kg of ash)

Note: 1 - respiratory, 2 - nervous, 3 - musculoskeletal, 4 - excretory, 5 - circulatory and lymphatic, 6 - digestive, 7 - integumentary, 8 - sensory, 9 - sexual, 10 - endocrine systems

Low concentrations of bromine in the nervous system may indicate the presence of a barrier that prevents penetration of the element. However, it is difficult to judge the endocrine system without analyzing other elements of the halogen group, or at the least, iodine, since bromine acts as its active competitor.

Thus, the content of bromine in plants and animals can vary significantly. In the plants of the Tomsk region, there are high concentrations of bromine (relative to other territories) in the Siberian clematis and birch tree. Low element concentrations in the nervous system of a domestic pig could indicate the presence of a serious biogeochemical barrier.

Features of bromine accumulation and distribution in the human body

The human body is a very complex system, representing the final link of the biogeochemical food chain, which can be considered as a geo-indicator integrating the transformation of the natural environment (Ignatova, 2010).

Levels of bromine accumulation in the blood of residents of the Tomsk region vary significantly in its different districts (Table 6.5). The settlement in which the

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 absolute maximum of the content of the element noted is Seversk city. A regularity is observed in the distribution in the Tomsky district, consisting of the presence of a spatial aureole with a well-defined north-eastern orientation (Figure 6.13).

Table 6.5 - Statistical parameters of the distribution of bromine levels in the blood of residents of the Tomsk region, mg/kg

District	N	X	λ	Min	Max	Mo	Me	V, %
Aleksandrovsky	5	19,7	2	13,8	25,4	–	20,2	22
Kargasoksky	4	22,9	3,4	14,6	30,9	–	23	–
Chainsky	1	8,4	–	8,4	8,4	–	8,4	–
Shegarsky	6	20,4	2,4	13,3	28,5	–	18,6	29
Kozhevnikovsky	3	14,7	2,7	10,7	19,8	–	13,6	32
Tomsky	133	30	4	4,2	434	12	21	153
Pervomaysky	3	27,2	4,5	19,2	34,7	–	27,6	29
Verkhneketsky	3	10,2	0,9	8,6	11,8	–	10,3	16
Zyriansky	62	12,4	0,5	6,2	24,1	8,3	11,5	33
Bakcharsky	35	20,5	0,9	11,8	34,6	15,9	19,9	27
Tomsk region	255	23,4	2,1	4,2	434	12	16,5	146

Note: N - number of samples; X - average value; λ - standard error; Min and Max - minimum and maximum values, respectively, Mo - mode, Me - median, V – variation coefficient.

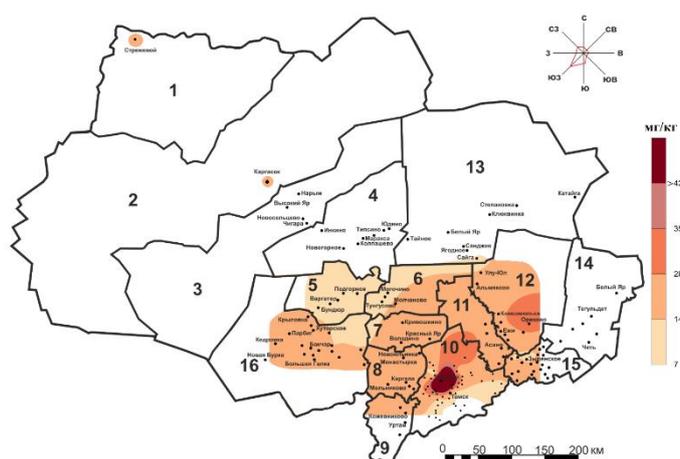


Figure 6.13 - Schematic map of the distribution of bromine (mg/kg) in the blood of residents of the Tomsk region

A comparison of our results on the level of accumulation of bromine in the blood of residents of the Tomsk region with data on other regions, as well as literature data, is shown in Figure 6.14. The content of bromine in the blood of residents of the Tomsk region exceeds those in the Republic of Kazakhstan, according to the available

literature and the results of studies conducted. However, they are lower than the concentrations of the halogen observed in the blood of Chelyabinsk region residents.

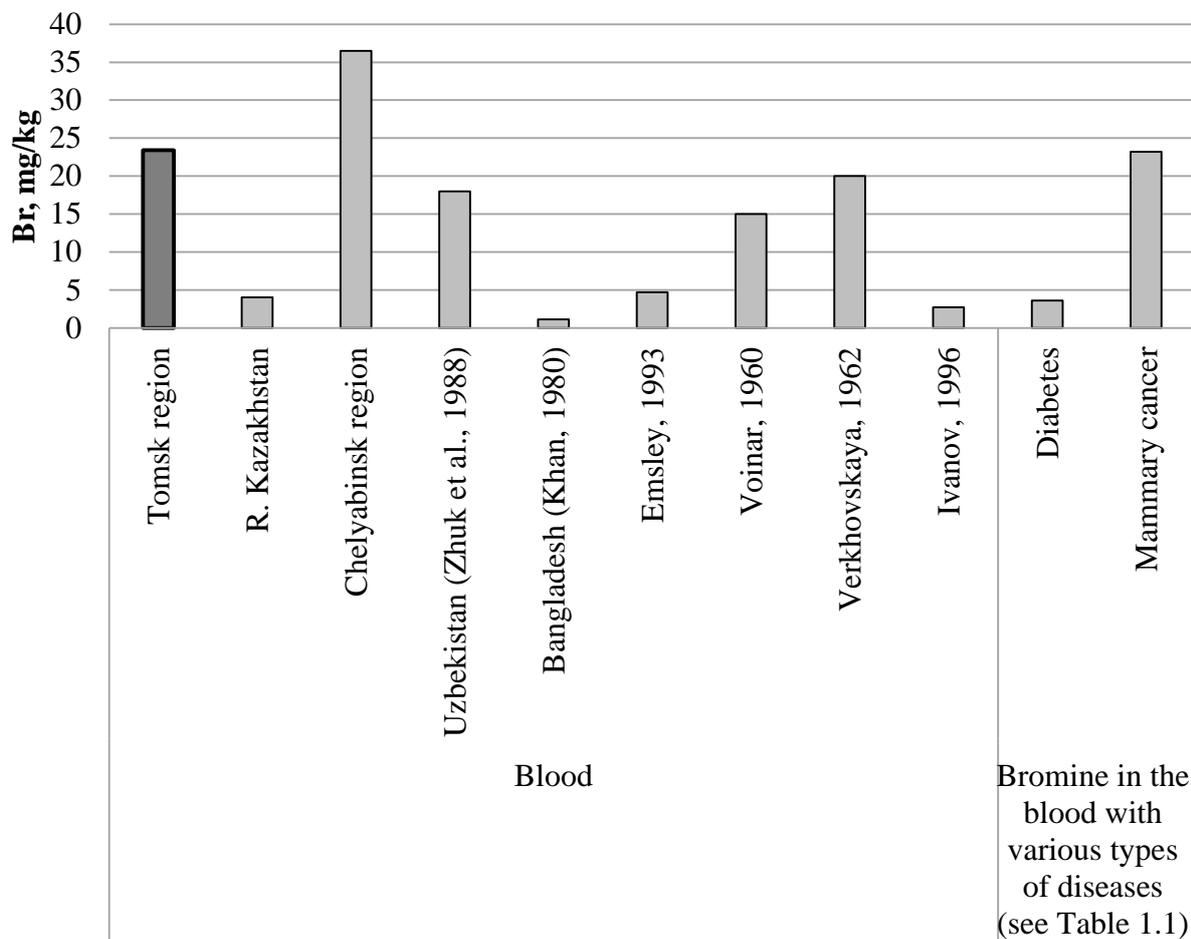


Figure 6.14 - The bromine content in the blood of residents of the Tomsk region and other regions of Russia and abroad (mg/kg of dry matter or ash)

The features of the spatial distribution of bromine in the children’s hair of the Tomsk region (Figure 6.15) are somewhat similar to those in the blood of the residents, which may indicate an identical entry pathway. Since bromine is a highly volatile element (*Emsley, 1991; Greenwood, 2008*), it very quickly penetrates into blood and hair through the respiratory tract and skin. We assume that identical features of the distribution of bromine in these biosubstrates indicate its preferential aerosol penetration way. This can also be judged by the increased levels of its accumulation in the respiratory system of the residents in the Tomsky district (*Baranovskaya et al, 2016*).

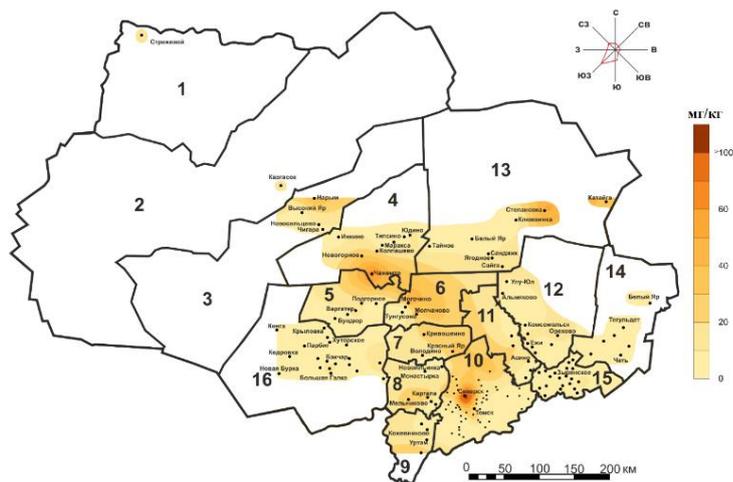


Figure 6.15 - Schematic map of the distribution of bromine (mg/kg) in the children's hair of the Tomsk region

In children's hair, there is another homogeneous geochemical field of the element, i.e. the absence of fluctuations in its content in the biosubstrate, among residents living upstream the Ob river and within the Kolpashevsky district of the region. This indicates, firstly, the multiple pathways of the halogen entering hair, which can be caused by both exogenous and endogenous pathways. The former is a transboundary transfer along the river valley, which apparently occurs as a result of the activities of industrial enterprises, located along the Tom river, which then flows into the Ob River. Endogenous pathways reflect the nutritional characteristics of the population, for example, the entry of the element with water, as well as through the trophic chains as a result of eating local river fish, etc. (*Baranovskaya, 2003*). In this case, we can speak of an inseparable connection between the former and the latter, and the direct influence of exogenous factors on endogenous ones. Secondly, it can be concluded that the chemical composition of the hair demonstrates the changes taking place in the environment under the influence of natural and man-made factors more clearly than blood. This fact was also noted by *N.V. Baranovskaya (2003)*.

The levels of bromine accumulation in the children's hair of the Tomsk region (Figure 6.16) exceed the data for all regions studied in Russia and abroad, with the exception of Canada (maximum values are indicated).

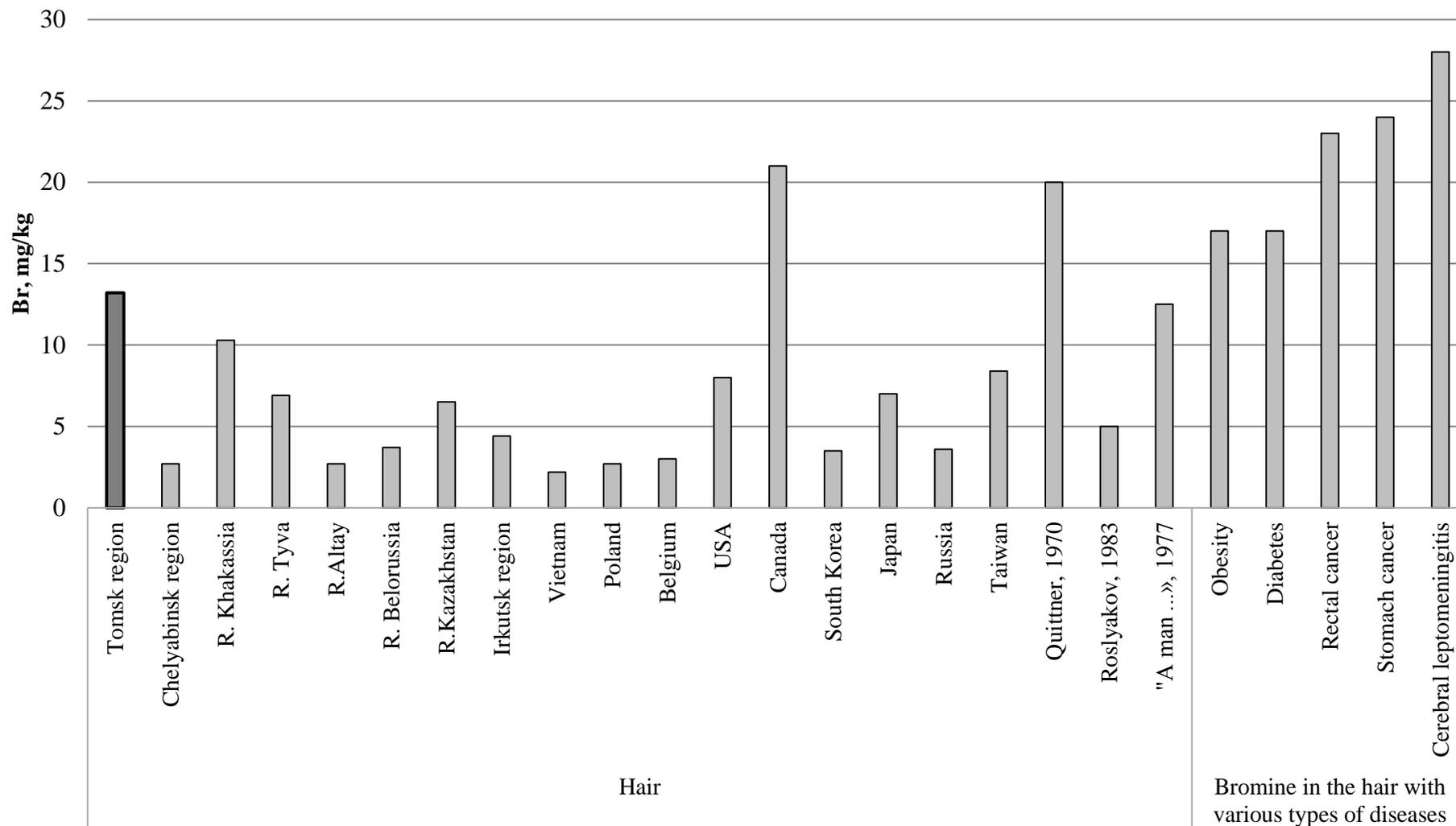


Figure 6.16 - Bromine content in the hair of residents of the Tomsk region and other regions of Russia and abroad, mg/kg

Note: for the comparative characteristics the data of Tables 1.1 and 2.6 were used

It should be noted that the content of bromine in the children's hair of the region is much greater than in the hair of children living in close proximity to the sea in such countries as Vietnam, the United States, Japan and a number of others, unlike the Tomsk region. However, the levels of bromine accumulation in the children's hair of the region are much less than its contents in the hair of sick people, suffering from stomach, rectum cancer, diabetes, etc. We assume that high levels of bromine concentration in the hair may indicate the presence of certain types of diseases, which cannot be judged by the content of the element in the blood.

As for the nature of bromine distribution in the pathologically altered thyroid gland, the cartographic information obtained shows that halos of the increased content of the element are found in several districts of the region: Aleksandrovsky, Kolpashevsky, Chainsky, Shegarsky and Tomsky (Figure 6.17). In general, it should be noted that the pathology of the thyroid gland of the population of the region requires special attention. A very important aspect in its formation may be bromine that has already been considered in detail in this paper. This issue is extremely important in the Tomsk region, which, according to *O.A. Denisova et al. (2011)*, is a biogeochemical province with iodine deficiency. It is noteworthy that there is a similar trend in the spatial distribution of the element in the thyroid gland and the hair, which consists of elevated concentrations of halogen in the biosubstrates of the inhabitants of Chazhemto city in the Kolpashevsky district of the region. In our opinion, it can be explained by the presence of a natural anomaly due to the presence of iodine - bromic mineralized waters. It should be emphasized that the hydrogeological conditions of the Kolpashevskaya formation are characterized by a number of specific features. There are deposits of cold waters of the Oligocene-Quaternary and Eocene-Upper Cretaceous complexes, warm waters of the Aptian-Albian-Cenomanian aquifer complex, hot waters of the Hauterivian-Barremian aquifer, very hot waters of the Valanginian aquifer Complex, as well as very hot and superheated waters of the Valanginian-Upper Jurassic, Lower-Upper Jurassic and Paleozoic aquifers (*Mishchenko M.V., 2007*).

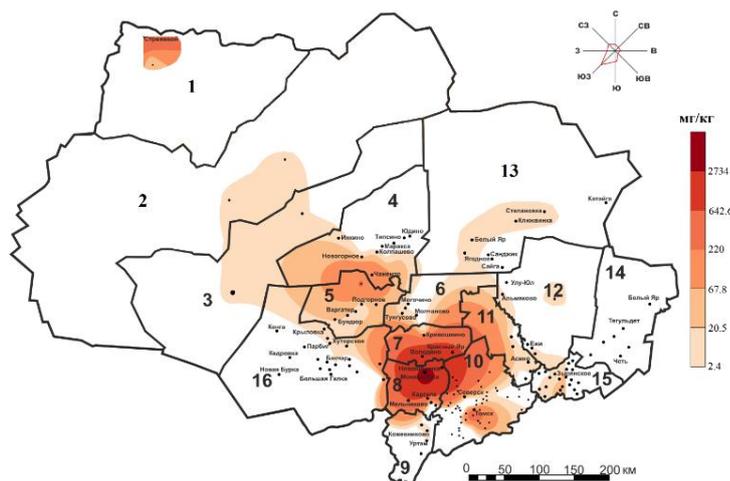


Figure 6.17 - Schematic map of bromine distribution (mg/kg) in the pathologically altered thyroid gland of residents of the Tomsk region

Anomalously high levels of bromine accumulation in this biomaterial are also noted in the glands of residents of the Aleksandrovsky district, which is not reflected in other environmental objects studied. Unlike the Aleksandrovsky district, in the Shegarsky district, where abnormally high concentrations of bromine in the thyroid glands of residents are recorded, elevated element contents are also noted in soils, scale of drinking water and in the children's hair. These discrepancies require additional research.

As the analysis shows, the concentration of bromine in the organs and tissues of the female body is higher than in the male body (Figure 6.18), which contradicts the literary data (*Verkhovskaya, 1962*). However, bromine concentrations in bronchi and lungs in the male body exceed those observed in the female body. This can be explained by physiological characteristics, since, on average, female lung volume is lower. For both sexes the highest content of bromine is found in the aorta. In general in the territory of the Tomsk region, we can note the contiguity of general trends in the accumulation of bromine in the organs and tissues of male and female organisms. The highest percentages of bromine are observed in the system of blood and lymph circulation, the lowest in the nervous system of both sexes. In any case, when the element enters the human body (by inhalation, oral or dermal ways) it is quickly distributed, but retained for a long time in the blood. That is why its maximum concentration is found in the blood and lymph circulation system.

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Particular attention should be paid to low concentrations of bromine in the human nervous system. This feature has already been observed in our studies on the domestic pig. Thus, this information is extremely important, because the question of the role of bromine in the evolution of the nervous system of living organisms was raised by *A.I. Perel'man (1979)*. The data we obtained, indicate a significant biogeochemical barrier in the nervous system of living organisms, which prevents the penetration of the element, despite its good migratory capacity noted for natural media.

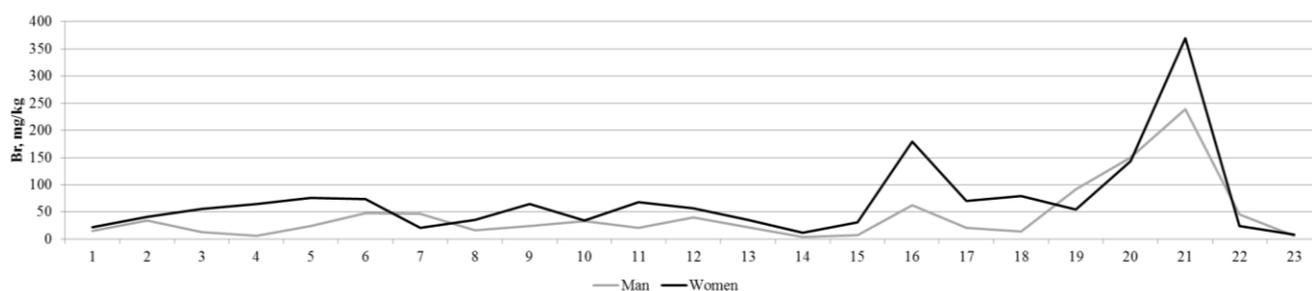
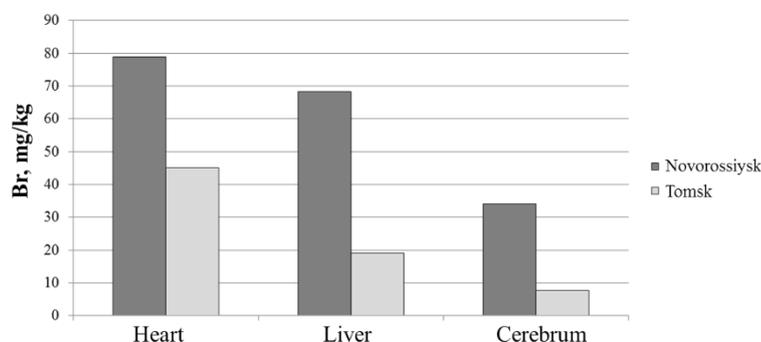


Figure 6.18 - Average bromine content in the ash residue of male and female organisms (mg/kg), living in the Tomsk region

Note: 1 - thyroid gland, 2 - small intestine, 3 - tongue, 4 - pancreas, 5 - stomach, 6 - bladder, 7 - bronchi, 8 - skin, 9 - duodenum, 10 - spleen, 11 - thick intestines, 12 - trachea, 13 - musculature, 14 - cerebrum, 15 - liver, 16 - esophagus, 17 - heart, 18 - adipose tissue, 19 - lungs, 20 - hollow veins, 21 - aorta, 22 - kidneys, 23 - nails.

Comparison of the ash residues of organs from cadavers of the Tomsk region and Novorossiysk (Figure 6.19) shows that in the organs of the inhabitants of the southern city the bromine content is much higher. This is due to the geographical location of the city and its proximity to the sea. In addition to receiving bromine from the air of this



"sea city", residents also consume large amounts of seafood that contain high concentrators of the element and contribute to its accumulation in the body.

Figure 6.19 - Average bromine content in the ash residue of the male and female body (mg/kg)

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The data obtained on the content of bromine in the human body, as well as knowledge of the general kinetic features of the element, made it possible to construct a simplified scheme of the mechanisms of entry, accumulation and distribution of the element in the body (Figure 6.20)., The mean levels of the ash residue from the Tomsky district (mg/kg) were taken as a basis for the data.

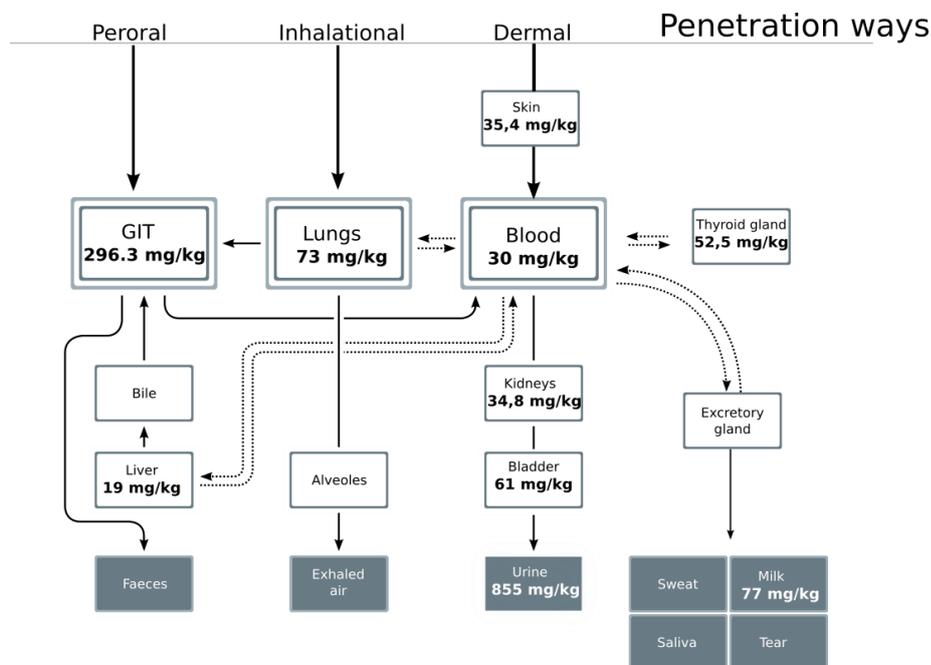


Figure 6.20 - Simplified diagram-figure of the intake, accumulation and distribution of bromine in the human body (mg/kg) based on the example of residents of the Tomsk region

It should be noted that the kinetic and dynamic features of bromine have been studied extremely poorly. Since the element is chemically active in biological systems, it is difficult to separate it from the compounds it forms in interaction with the moist surface of the mucous membranes, respiratory tract tissues, as well as the gastrointestinal tract. In living tissue, bromine rapidly passes into bromide and remains in the tissues in this form (*Verkhovskaya, 1962*). Most of the bromine enters the body by the oral route. In addition, the element is a constant part of normal gastric juice. Bromine, which enters the gastrointestinal tract by blood, is sent to the liver, which is the main organ where the complex organic compounds of bromine are destroyed. From the liver, it is excreted through the intestine, together with bile, while a part of the element can be reabsorbed into the blood and excreted in the urine. Another way to get

bromine into the body can be inhalation, since bromine is a highly volatile element it quickly penetrates the respiratory tract and then the bloodstream. Some of bromine can enter the stomach with saliva, while the rest is expelled from the body by exhalation. The third way the element penetrates into the body is via skin, damaged skin tissues are especially sensitive. Bromine, penetrating through the skin, immediately enters the blood. However, as with any type of bromine intake into the body, its distribution passes quickly, and then it stays in the blood for a long time, which indicates that the element is practically not included in the exchange between organs and tissues. Bromine is mainly lost through urine, but a small amount of the element can also be eliminated with feces, saliva, milk and tears.

Since most bromine enters the body by the oral route, i.e. with food and drink (*Verkhovskaya, 1962*), the study of food products consumed by the inhabitants of the region is extremely important. In addition, the analysis of the ecological and geochemical situation cannot be considered complete without studying the data on nutrition and the chemical composition of foods consumed by the population (*Pokatilov, 1992*). Food is one of the most important factors of normal functioning and a vital activity of living organisms, providing them with necessary substances and elements. Since the main entry way of chemical elements into the human body is precisely the oral (from 80 to 95% with food, 4.7% - with water), mainly with plant and animal food as a result of its passage through food chains, then some elements can be closely related to a human's health, causing physiological or metabolic changes. Hippocrates also noted this relationship, saying: "Tell me what you eat, and I'll tell you what you're sick of." In Russia, a great contribution to the study of the role of chemical elements for living organisms was made by Voinar A.O, Gabovich R.D., Kolomiitseva M.G., Nozdryukhina L.R., Peive Y.V., Khakimova A.M., etc.

Unfortunately, the microelement composition of food products has not yet been studied in great depth. Studies in general for the Russian Federation, and in particular in Siberia, are focused mainly on the study of heavy metals (primarily mercury, cadmium, lead, arsenic, zinc, copper, tin and iron, which were identified as priority, in

Chapter 6. Peculiarities of bromine accumulation and distribution in the environmental compartments of the Tomsk region accordance with international requirements FAO/WHO), iodine (due to the lack of that element observed in many regions of Russia) and radionuclides (*Bogachev, 2001; Dryutskaya, 2005; Shitova, 2005; Zakharova, 2006, etc.*). However, data on other essential elements, including bromine, is practically absent. Thus, for the first time, we carried out a comprehensive analysis of food products, consumed by people living in the Tomsk region.

As shown in the review chapter, the content of bromine in products of different regions of the world varies widely (Table 2.8), and, therefore, the daily consumption of bromine by the inhabitants of different countries differs significantly (Table 2.7). The food products of the Tomsk region we studied (Figure 6.21) demonstrate that the highest levels of bromine accumulation are marked (in descending order): in coffee, milk, pork, rice, pasta, etc. The smallest content of the element is noted in buckwheat.

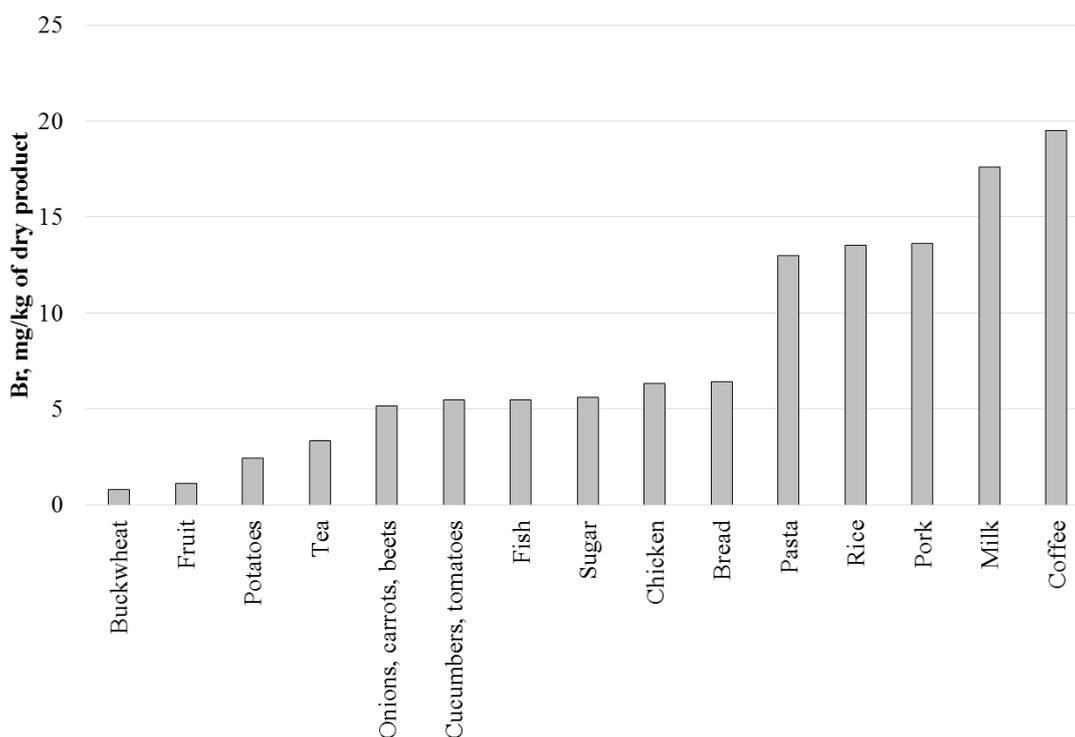


Figure 6.21 - Bromine content in food products (mg/kg of dry product)

At the same time, a comparative analysis of bromine content in food products, consumed in the Tomsk region and by residents of other countries (Figure 6.22) demonstrates that in comparison with other regions, higher levels of bromine are observed in milk, rice, onions and chicken eaten in the Tomsk region.

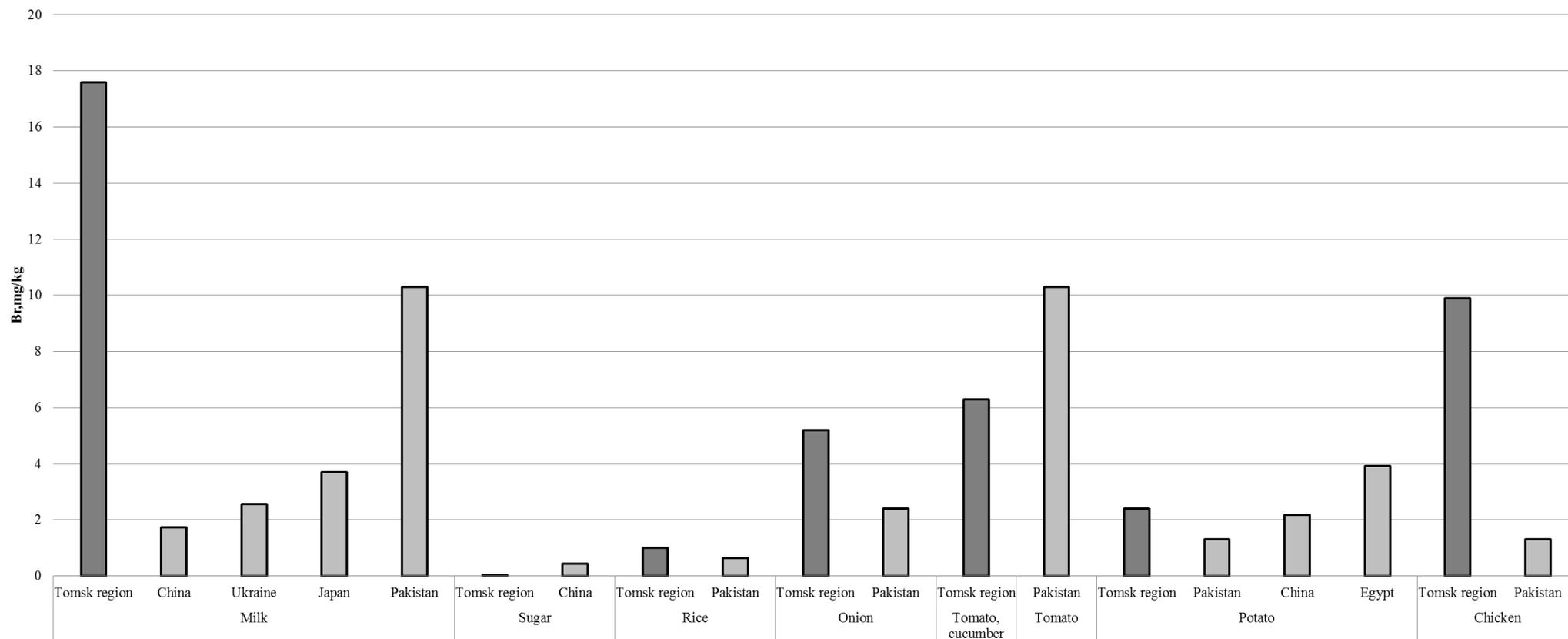


Figure 6.22 - Comparative analysis of bromine content in food products (mg/kg of dry product), consumed by residents of the Tomsk region and residents of other countries

For the comparative analysis, the data of Table 2.8 were used

Chapter 6. Peculiarities of bromine accumulation and distribution in the environmental compartments of the Tomsk region

Thus, the distribution of bromine in blood, children's hair and pathologically altered thyroid glands of Tomsk region residents is extremely uneven. Analysis of the material selected in different territories along with the literature data indicates rather high levels of accumulation of the element in the biosubstrates of the inhabitants of the Tomsk region. In the human body, as in the domestic pig's organism, low levels of bromine accumulation in the nervous system are noted, which may indicate the presence of a biogeochemical barrier preventing bromine penetration in a given system of living organisms, despite its good migratory capacity noted for natural media. In food products consumed by residents of the Tomsk region, the highest bromine content is observed in coffee and milk, and the smallest in buckwheat.

The studied factual data allowed us to determine the most tense the areas most at risk in the Tomsk region in accordance with the peculiarities of the distribution of bromine in the environmental compartments (Figure 6.23). Based on the information on the halogen content in the studied objects, we proposed a differentiation of areas in accordance with the levels of bromine accumulation in the environmental components.

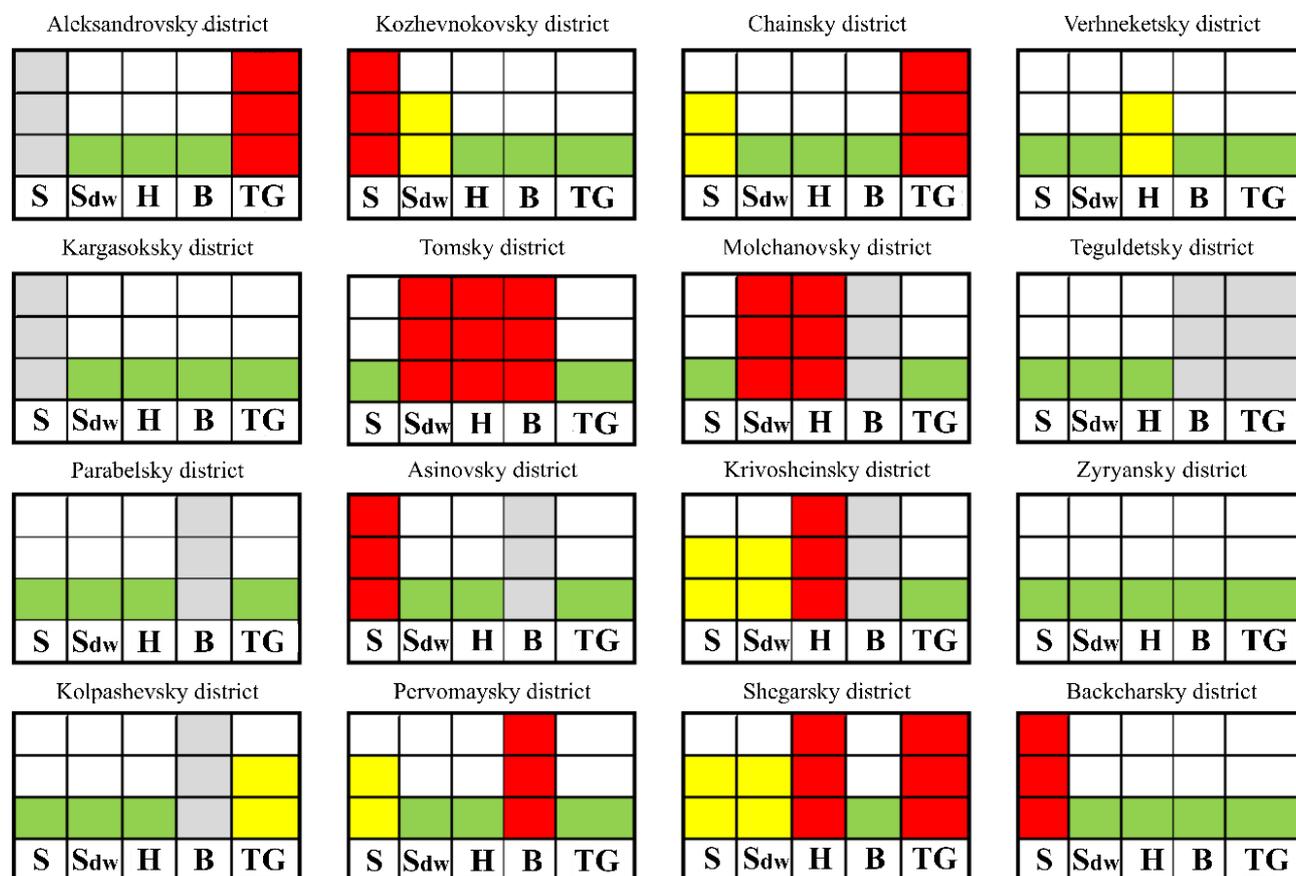


Figure 6.23 – Schemas according to the distribution of bromine in the components of the environment, where *S* is the soil, *S_{dw}* is the scale of drinking water, *H* is the hair, *B* is the blood, *TG* is the pathologically altered thyroid gland

Note: green means low element content that does not exceed the average regional values; yellow mean average concentrations of the element, or close to that; red color shows increased levels of bromine accumulation, significantly different from the average; gray indicates lack of data.

The analysis allows us to consider the balance of the distribution of bromine within the compartments of the Tomsk region studied (Figure 6.24). Due to the specific features of the territory (for example, considerable distance from the sea), we cannot include in our analysis some environmental components that, on a global scale, certainly influence the accumulation of bromine, but whose role on the local scale is less significant. Since the Tomsky district of the region is the most affected by bromine, and due to the presence on its territory of a large number of potential anthropogenic bromine sources mainly in its northern sections, we did not take into account the actual material selected in the Northern Industrial Zone. The red color indicates those components of the environment, biosubstrates, etc., whose bromine content exceeds the literature data shown in Figure 2.3.

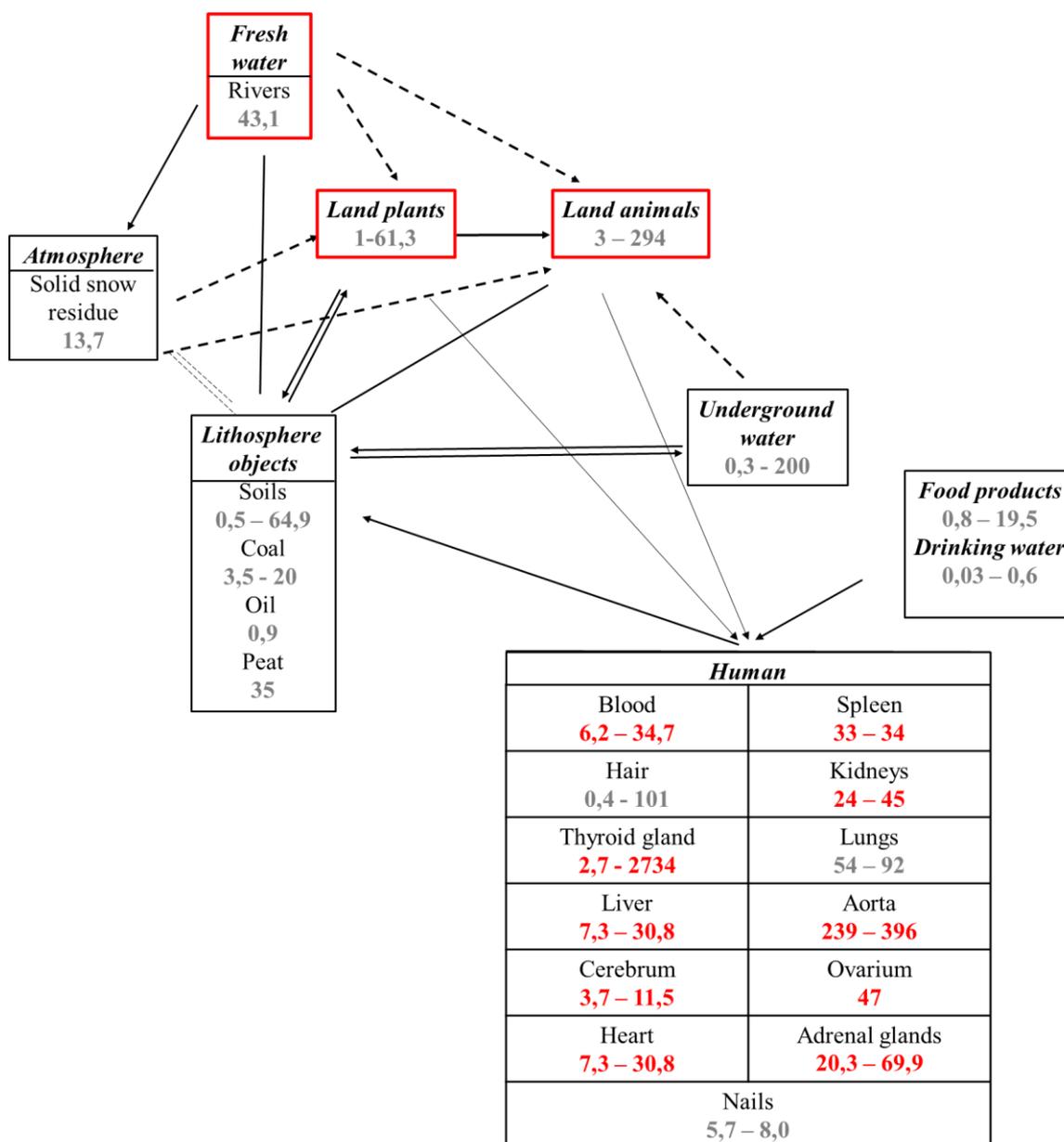


Figure 6.24 - Simplified scheme for the distribution of bromine in the environment of the Tomsk region within the normal cycle of the element in nature, in mg/kg (for hydrosphere objects - in mg/l)

Note: data on fresh and underground waters is from Kolubaeva, 2015 (according to the author the water data corresponds to a background level and is regarded as characteristic of ecologically clean areas); solid sediment of snow (background regions of Western Siberia) - according to Shatilov, 2001; peat - according to Mezhibor, 2009, oil - according to Rikhvanov et al., 2015.

Brief conclusion

Thus, the information on the levels of bromine accumulation in the components of the environment of the Tomsk region allows us to conclude that the abiotic components are characterized by homogeneity in the accumulation of the element, in contrast to the biotic ones. In general, in comparison with the literature data, for the territory of the Tomsk region significantly higher bromine levels are observed in fresh waters and its accumulation in terrestrial plants in concentrations above 60 mg/kg and in animal organisms at about 300 mg/kg. A high content of the element is also observed for the human body, but its concentration is observed not in the hair and lungs, but more in the blood, kidneys, aorta, thyroid, etc.

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**CHAPTER 7. BROMINE UNDER THE CONDITIONS OF
TECHNOGENESIS (ON THE EXAMPLE OF THE
TOMSKY DISTRICT OF THE TOMSK REGION)**

Chapter 7. Bromine under the conditions of technogenesis (on the example of the Tomsky district of the Tomsk region)

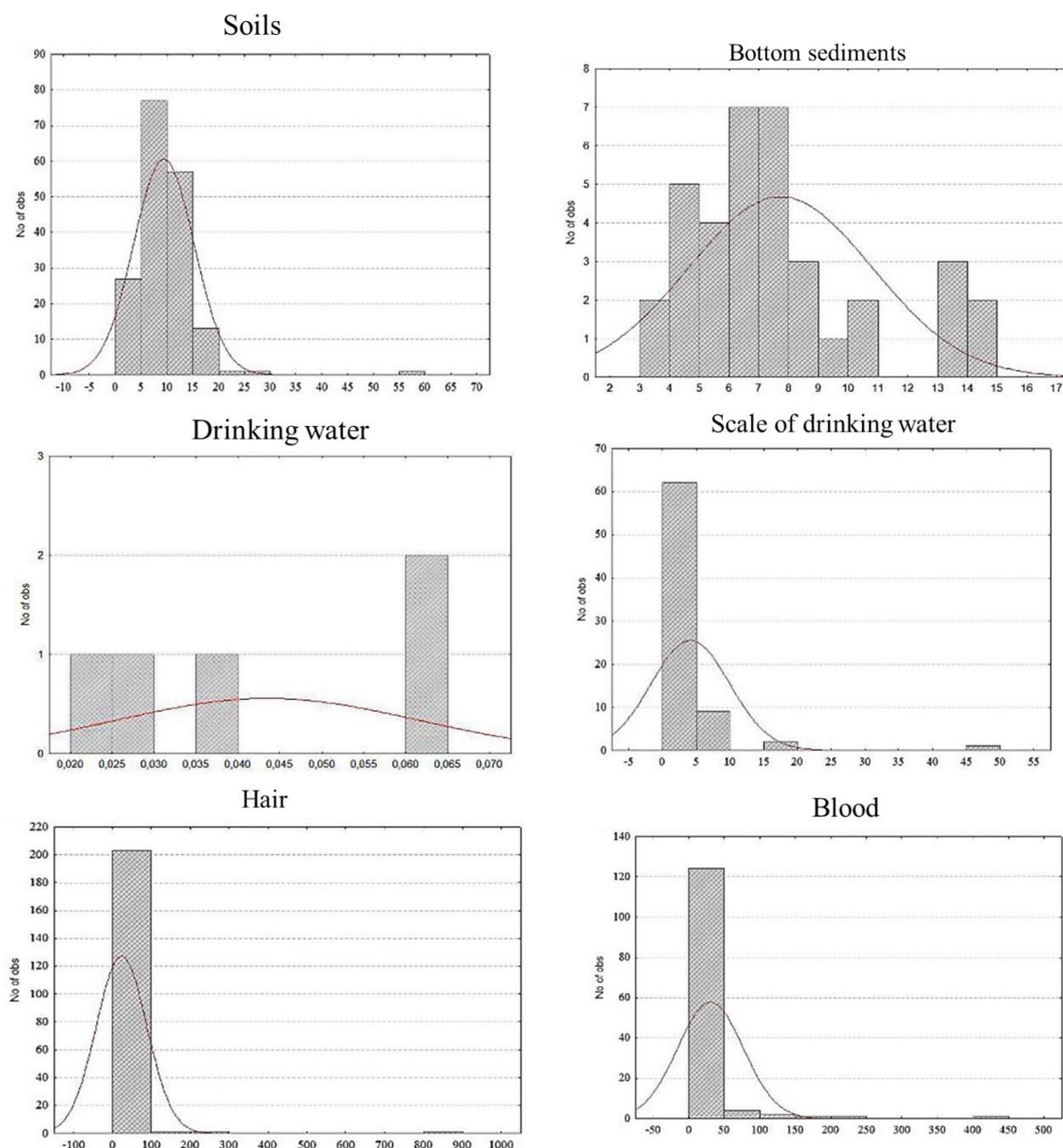
The peculiarities of bromine concentration in environmental objects under conditions of technogenesis are very poorly studied and require particular attention (Ivanov, 1996). The Tomsky district of the region, in our opinion, can serve as an example for the analysis of the element's technological geochemistry, since the main industrial centers of the Tomsk region are concentrated in its territory (the Northern Industrial Zone or the Tomsk-Seversk agglomeration), including potential sources of the halogen (see Chapter 5). Despite the special interest in this area, in practice, the ecological and geochemical features of bromine within it have not been studied. In many works devoted to its study, the halogen is considered along with other chemical elements, without focusing on the detailed patterns of its accumulation and distribution in the environment. Bromine is partially considered in the work of *E.G. Yazikov (2006)*. Perhaps the only study aimed at detailed specification and analysis of bromine is the research of *N.V. Baranovskaya (2003, 2011)* and *E. Terpak (2008)*. On the basis of studies of the blood and hair of the inhabitants, *N.V. Baranovskaya (2003)* showed that within the Tomsk-Seversk agglomeration, a stable bromine subprovince of a natural-technogenic character is formed. In addition, the results of the studies demonstrate that, approaching the industrial zone, bromine concentrations increase in cow's milk (*Boyarkina et al., 1980*), in the children's hair (*Baranovskaya, 2003*) and in the solid snow sediments (*Shatilov, 2001*). In addition, Br/U ratios in the children's hair have an analogy with the change in ^{137}Cs concentrations in soils within the industrial zone (*Baranovskaya, 2002*).

To analyze the changes in bromine content in the environment in close proximity to the Tomsk-Seversk agglomeration, we have grouped all the settlements of Tomsky district according to two principles. The first principle is based on a division of the settlements by the sectors of influence of the Tomsk-Seversk agglomeration, taking into account the prevailing direction of the wind. Thus, the north-eastern, north-western, south-eastern and south-western sectors are identified. The second is based on the distance from the agglomeration, the first group includes settlements that are within the 30 km zone of industrial influence, the second – over 30 km away. This kind of

Chapter 7. Bromine under the conditions of technogenesis (on the example of the Tomsky district of the Tomsk region)

division of settlements into groups is not new and has already been used in a number of works (*Shatilov, 2001, Yazikov, 2006*), and partially in the work of *D.V. Narkovich (2012)*.

The histograms of the distribution of bromine content in the studied objects in the Tomsk region (Figure 7.1), together with the statistical parameters (Table 7.1), indicate a non-normal distribution of the element in the environmental objects. It is only close to normal for soils and bottom sediments.



Chapter 7. Bromine under the conditions of technogenesis (on the example of the Tomsky district of the Tomsk region)

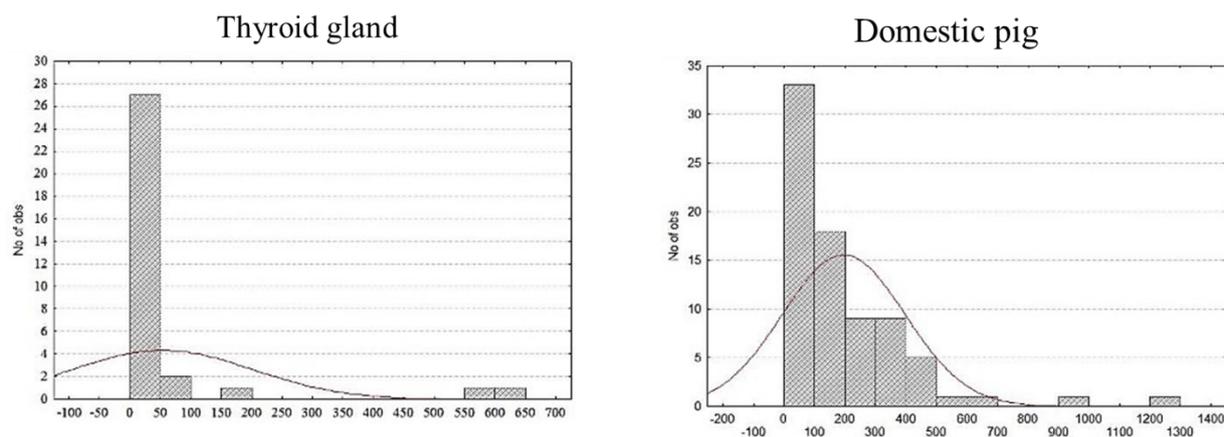


Figure 7.1 - Histograms of the distribution of bromine in the environmental components of the Tomsky district (mg/kg, mg/l for drinking water)

Minimal variation coefficients are observed for bromine in bottom sediments, drinking water and soils, and are 40%, 41%, 65%, respectively. The maximum values of the variation coefficient are observed in the pathologically altered thyroid gland (280%) and in children's hair (290%), indicating a highly heterogeneous distribution of the element in these biosubstrates.

Table 7.1 - Statistical parameters of the distribution of bromine content in the environmental components of the Tomsky district, mg/kg

Research object	N	X	λ	Min	Max	Mo	Me	V,%
Soils	182	9,1	0,4	0,5	59,5	0,5	8,9	65
Bottom sediments	36	7,7	0,5	3,4	14,9	7,4	7,2	40
Drinking water, mg/l	5	0,04	0,008	0,025	0,06	–	0,04	41
Scale of drinking water	83	3,8	0,6	0,2	47,7	0,5	2,8	144
Children's hair	207	16,7	1,0	0,3	895	13,0	13,0	290
Blood	133	30,0	4,0	4,2	434	12,0	21,0	133
Thyroid gland (pathologically altered tissues)	32	8,1	2,0	2,2	619	5,4	5,4	280
Organs and tissues of domestic pig	78	194	22,7	5,5	1204	–	123,3	103

Note: N - number of samples; X - average value; λ - standard error; Min and Max - minimum and maximum values, respectively, Mo - mode, Me - median, V - variation coefficient.

7.1. Bromine in abiotic components of the environment

Soil and bottom sediments. Against the background of the entire Tomsk region, the Tomsky district is characterized by the lowest content of bromine in the soils, but the highest scatter of minimum - maximum values is noted (Table 6.1), which indicates the presence of factors that significantly distort the background distribution of the element. According to previous studies (*Yazikov, 2006*), the highest levels of halogen in soils are found near the Tomsk petrochemical plant, located in the zone of influence of the Tomsk-Seversk industrial agglomeration. As for Tomsk city, high levels of bromine accumulation are observed near such industrial enterprises as "Pharmstandard-Tomskkhimfarm", «Tomsk Instrument Plant» and «Tomsk Electric Lamp Factory» (*Zhorneyak, 2009*).

Analysis of changes in the content of bromine in the Tomsky district over time, demonstrates that in recent years there has been a significant decrease in the accumulation of the element in soils. This is also typical for individual settlements, including those located in the industrial zone (Figure 7.2). At the same time, in soils selected in 2005 and 2006, significant positive correlations of bromine with Sm and Tb are noted, and with Sr in soils from 2014, which indicates a change in the geochemical situation in the soils at the territory of the district.

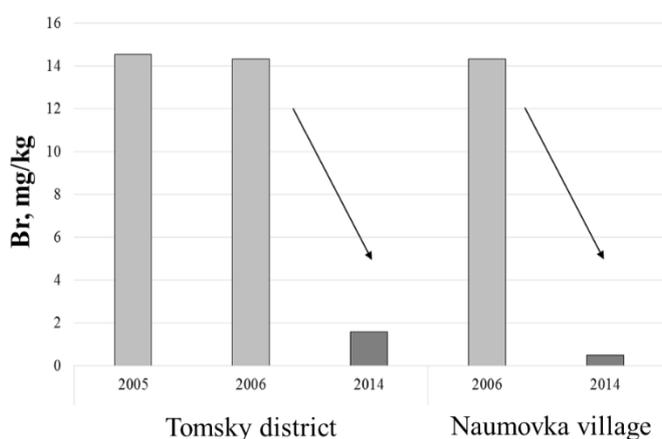


Figure 7.2 - Changes over time in the content of bromine in the soils of Tomsky district and in the village of Naumovka, mg/kg

In the dynamics of bromine change, depending on the remoteness from the zone of the Tomsk-Seversk industrial agglomeration, no tendency to decrease or increase is

Chapter 7. Bromine under the conditions of technogenesis (on the example of the Tomsky district of the Tomsk region)

observed within different years, the levels of bromine accumulation at different distances are almost identical.

In the work of *N.V. Baranovskaya (2011)* the dynamics of bromine change in the soils of the Chelyabinsk region, where the nuclear fuel cycle enterprise "Mayak" is situated (similar to the Siberian power plant in the Tomsk region) but there are no large oil refining complexes, were analyzed. It was shown that the content of bromine in soils decreases with distance from this industrial enterprise. In 2014, we conducted comprehensive studies in France, in the Grand Est region, where there is a large oil refinery. As the results show (Figure 7.3), the levels of accumulation of bromine (bromide ion) in soils also tend to decrease with distance from the industrial complex.

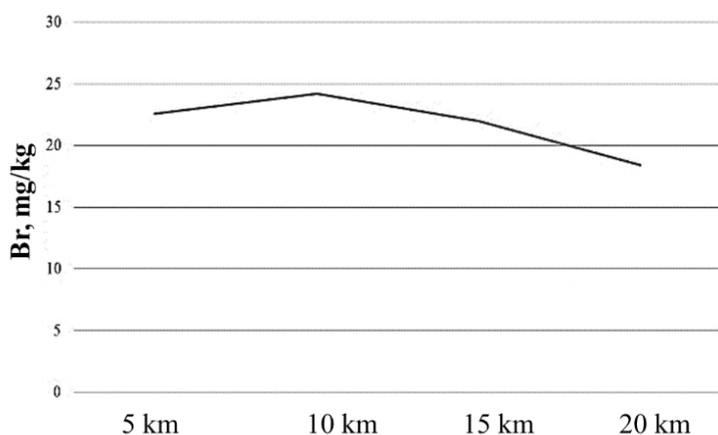


Figure 7.3 - Change in Br⁻ content in soils of France while moving away from the refinery, μg/kg

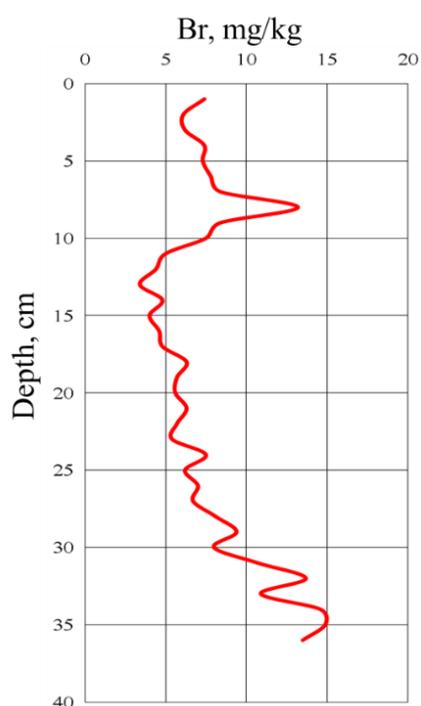
This also results in a decrease in the Br⁻/I⁻ ratio, but an increase in Br⁻/F⁻ at a distance from the refinery. However, the Br⁻/Cl⁻ ratio is stable (Table 7.2).

Table 7.2 - Changes in bromine ratios with other elements of the halogen group in soils at different distances from the refinery (France)

Distance from oil refinery, km	Br ⁻ /F ⁻	Br ⁻ /Cl ⁻	Br ⁻ /I ⁻
5	0,0041	0,002	174
10	0,0042	0,002	173
15	0,0042	0,002	157
20	0,0058	0,002	142

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For the example of bottom sediments, collected in the Chernoye lake, located northeast of Tomsk in the zone of direct influence of the Siberian Chemical Combine (Ivanov, 2016), peaks of the increased concentrations of the element are recorded, observed at a depth of 10 cm, and also starting from a depth of 30 cm (Figure 7.4). The



distribution of bromine in the sediments does not coincide with any of the other 28 chemical elements studied. In the bottom sediments of this lake, there are significant positive correlations of bromine with practically all chemical elements (Sm, Lu, U, Yb, As, Na, La, Ce, Th, Cr, Hf, Ba, Ag, Cs, Sc, Tb, Rb, Fe, Ta, Co, Eu, Sb) and significant negative correlations with Ca and Sr, which may indicate the possible impact of both natural and anthropogenic factors.

Figure 7.4 - Distribution of bromine in the bottom sediments of the Black lake with depth, mg/kg

Thus, despite the low content of bromine in the soils of the Tomsky district, they are characterized by the largest scatter of minimum-maximum values. The accumulation of bromine in soils has tended to decrease in recent years, with a change in the geochemical situation as a whole. Analysis of the study of bromine in French soils shows a decrease in the content of the element while moving away from the oil refinery, with a parallel decrease in the Br^-/F^- ratio and an increase in the Br^-/Cl^- ratio, with a fixed stability of the ratio Br^- to Cl^- . In the bottom sediments, elevated element contents are noted at a depth of 10 cm and below 30 cm, while significant geochemical associations of bromine are observed with practically all the elements studied.

Drinking water and drinking water scale. Levels of accumulation of bromide - ion in drinking waters of settlements of the Tomsky district do not exceed the maximum permissible concentration for the element. The lowest content of bromine is observed

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in the waters of the village Zonal'naya stantsiya, and the largest, exceeding the average regional content, in the villages of Kopylovo and Kuzovlevo (Figure 7.5 left). The minimum Br⁻/I⁻ ratio is observed in the village Samus, and the maximum in the village Kopylovo (Figure 7.5 on the right). In the drinking waters of the Tomsky district, bromine is characterized by a significant negative correlation with chromium.

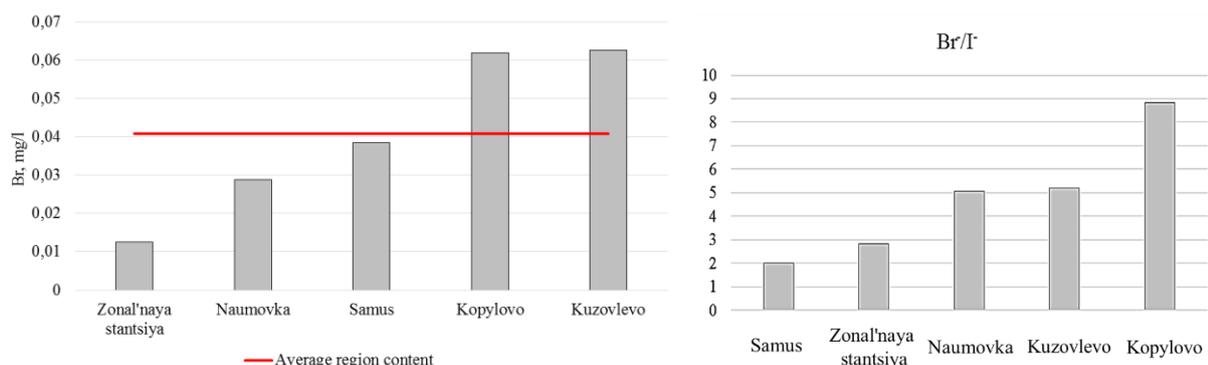


Figure 7.5 - Ranking of settlements of Tomsky district according to the level of accumulation of bromide ion in drinking water, mg/l (left) and Br⁻/I⁻ (right)

The bromine content in the scale of drinking water of the Tomsky district is characterized by increased element content, relative to other areas of the region, and also by a rather high scatter of minimum-maximum values, with a variation coefficient of 144% (Table 7.1). Elevated concentrations of bromine in the scale of drinking water are observed in 35 of the 43 settlements we considered in this area (Figure 7.6).

The question of the content of halogen in the scale of drinking water was partially discussed in the work of *E.G. Yazikov (2006)* and *T.A. Mongolina (2011)*. Unfortunately, in the first author's work, no explanation is found for the spatial localization of bromine. According to *T.A. Mongolina* the sources of the element are the petrochemical combine and the Siberian Chemical Combine, located within the district. Analysis of the available information also allows us to make an assumption about the predominant effect on the accumulation of the element in the scale of a given area by technogenic factors, which is clearly expressed when considering the correlations of bromine.

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In the Tomsky district, significant correlations of bromine with rare-earth elements in the scale of drinking water are observed: La, Sm, Eu, Lu, Yb, Tb (Figure 7.7), typical for enterprises of the nuclear fuel cycle, to which only the Siberian Chemical Combine belongs.

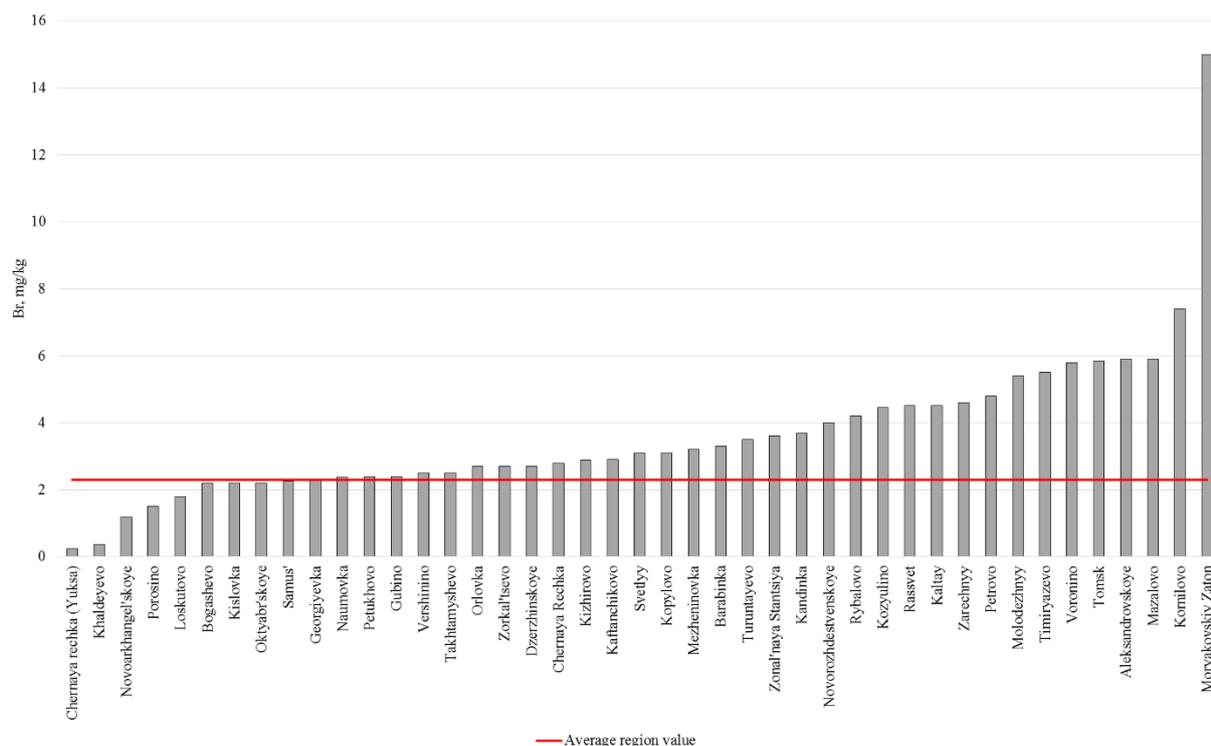


Figure 7.6 - Ranking of settlements of the Tomsky district according to the Br content in the scale of drinking water, mg/kg

It is noteworthy that in the scale of drinking water taken from the residents living near the Mayak nuclear power plant fuel complex in the Chelyabinsk region, there are also significant geochemical associations of bromine with lanthanum, which gravitate towards Lu and Sm (Figure 7.8).

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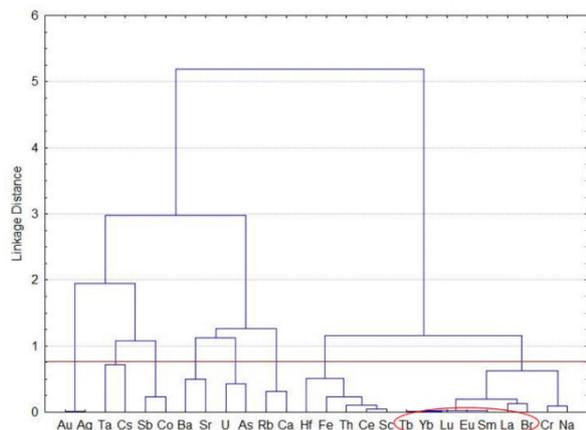


Figure 7.7 - Dendrogram of the correlation matrix of the geochemical spectrum of elements in the scale of drinking water in the Tomsk region ($1\text{-Person } r(0.05) = 0.89$, sample size - 83 samples)

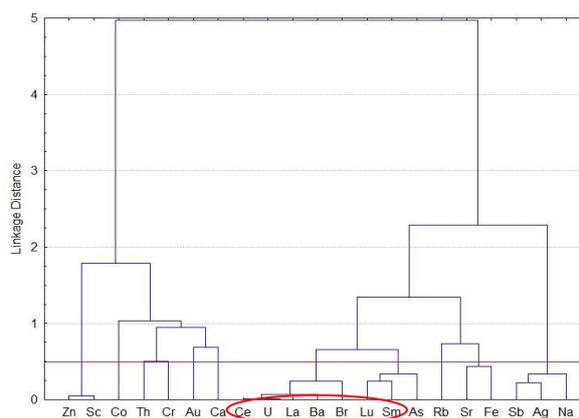


Figure 7.8 - Dendrogram of the correlation matrix of the geochemical spectrum of elements in the scale of drinking water in the Chelyabinsk region ($1\text{-Person } r(0.05) = 0.49$, sample size - 15 samples)

However, we should not exclude the impact of another natural-anthropogenic factor. A local hydrochemical anomaly is found in the zone of the Ob-Tomsk interfluvium, within which 16 of the 43 settlements we study are located (including the settlement of Moryakovskiy Zaton, where the absolute maximum of bromine content is found in the scale of drinking water). It consists of irregular occurrences over time, of discrepancies in the quantities of sodium and chlorine, accompanied by increased water salinity. According to some scientists, this anomaly is associated with the operation of the Tomsk water intake, which led to a decrease in the pressure of the waters of the Paleogene complex and, as a consequence, flows of water from the lower Upper Cretaceous complex (Kolubaeva, 2015). Direct information indicating an increased concentration of bromine in a given area due to the anomaly described above is not available. However, it can be assumed due to several reasons. Firstly, bromine concentrations, as a rule, increase with increasing mineralization and with the depth of occurrence of aquifers (Ivanov, 1996; Krasintseva, 1968; Rosen, 1970). Secondly, the bromine concentrations usually increase in parallel with the increase in the total amount of chlorine (Rosen, 1970). In addition, the research of Gurevich I.V. (1961), based on

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an analysis of more than 300 groundwater samples, show a clear relationship between the Na/Cl and Cl/Br coefficients (*Rosen, 1970*).

The dynamics of bromine change in the scale of drinking water shows that the concentration of the element decreases as it moves away from the impact zone of the Tomsk-Seversk industrial agglomeration (Figure 7.9).

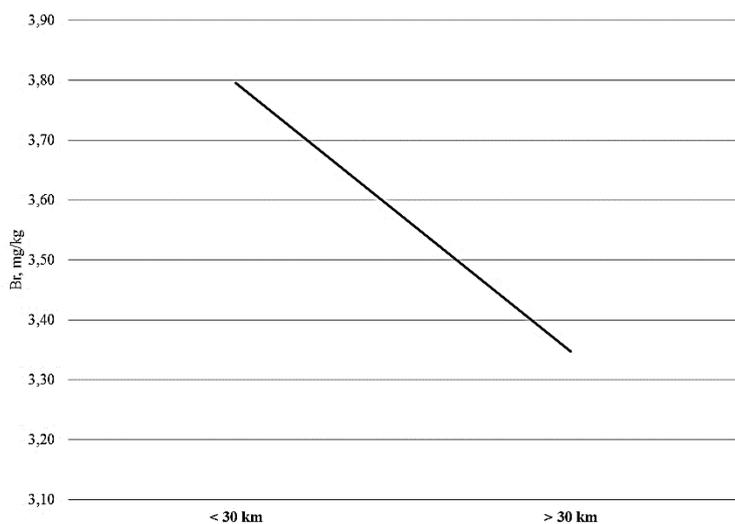


Figure 7.9 - Bromine content in the scale of drinking water when moving away from the Tomsk-Seversk industrial agglomeration

This trend persists in all directions, except for the south-western sector (Figure 7.10), in which the hydrochemical anomaly described above is situated.

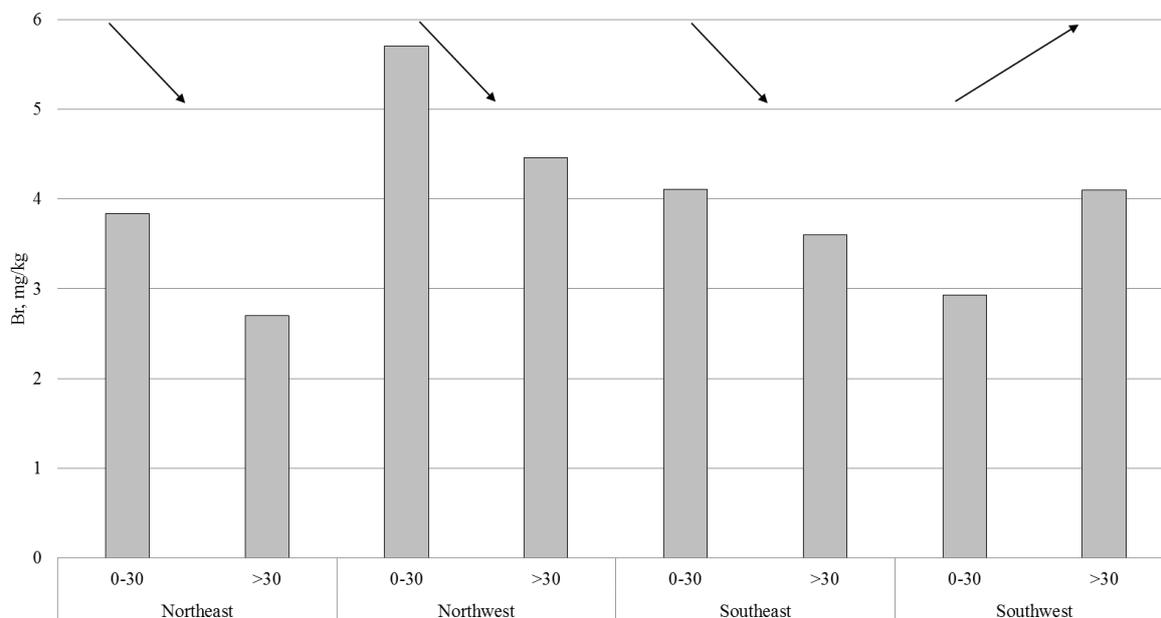


Figure 7.10 - Bromine content in the scale of drinking water when moving away from the Tomsk-Seversk industrial agglomeration by sector

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The correlation analysis, carried out according to the analytical data selected in 2014, demonstrates the presence of positive significant correlations between bromine and sodium, iron, arsenic, cesium, lanthanum, europium, hafnium, thorium and uranium in the scale of drinking water, which is somewhat different from the correlations observed in previous years (Figure 7.7), while significant positive links with Eu and La remain.

Thus, the content of bromine in drinking water in settlements of the Tomsky district does not exceed the maximum permissible concentration for the element. The content of the halogen in the drinking water scale of the district is characterized by higher concentrations than other areas. The maximum quantity of the element is observed in Moryakovskiy zaton village. The marked significant correlation of bromine in the scale of drinking water in the district indicates the influence of the nuclear fuel cycle enterprise, and is similar to that characteristic of the Chelyabinsk region. In general, there is a decrease in the content of the element as we move away from the industrial zone, with the exception of the south-western sector in which a natural-technogenic hydrochemical anomaly is found.

7.2. Bromine in biotic components of the environment

Children's hair. The results of the study of bromine in children's hair in the Tomsky district show that the spatial distribution of the element is uneven, as indicated by the statistical indicators (Table 7.1). For example, the variation coefficient is maximum for this district and represents 290%. Analysis of bromine accumulation in children's hair in the Tomsky district shows the highest levels of concentration of the element in the hair of the inhabitants of Seversk, Zonal'naya stantsiya, Chernaya rechka (Yuksa), etc. (Figure 7.11).

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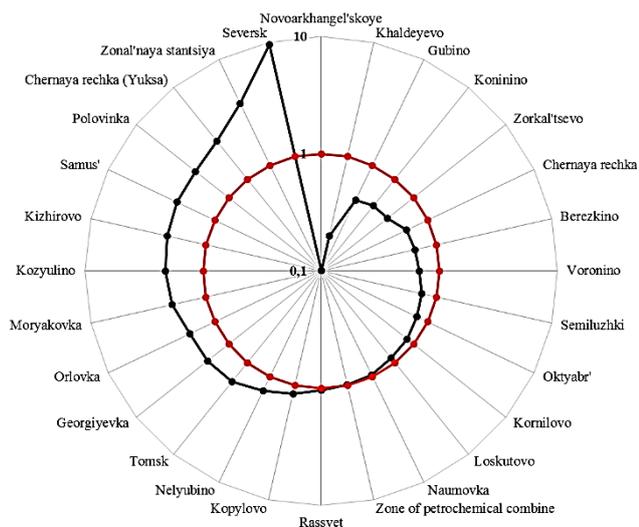


Figure 7.11 - Coefficients of bromine concentration in the children's hair, living in the settlements of the Tomsky district relative to the average regional values

When analyzing the behavior of the element in children's hair with the distance from the main industrial objects of the industrial zone, as in the drinking water scale, the concentration of the element also decreases (Figure 7.12).

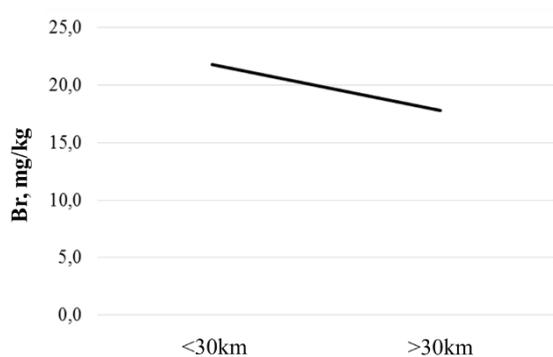


Figure 7.12 - Content of bromine in children's hair with the distance from the Tomsk-Seversk industrial agglomeration

When considering the changes in the content of bromine in children's hair, as well as the correlation of the halogen with other chemical elements in the sectors of the Tomsky district (Figure 7.13), there is a similar pattern in the northeast and north-western sectors, which consists of a reduction in the content of the element when moving away from the Tomsk-Seversk industrial agglomeration. As for the other two sectors, we cannot judge the changes in the accumulation of the element due to the lack of data.

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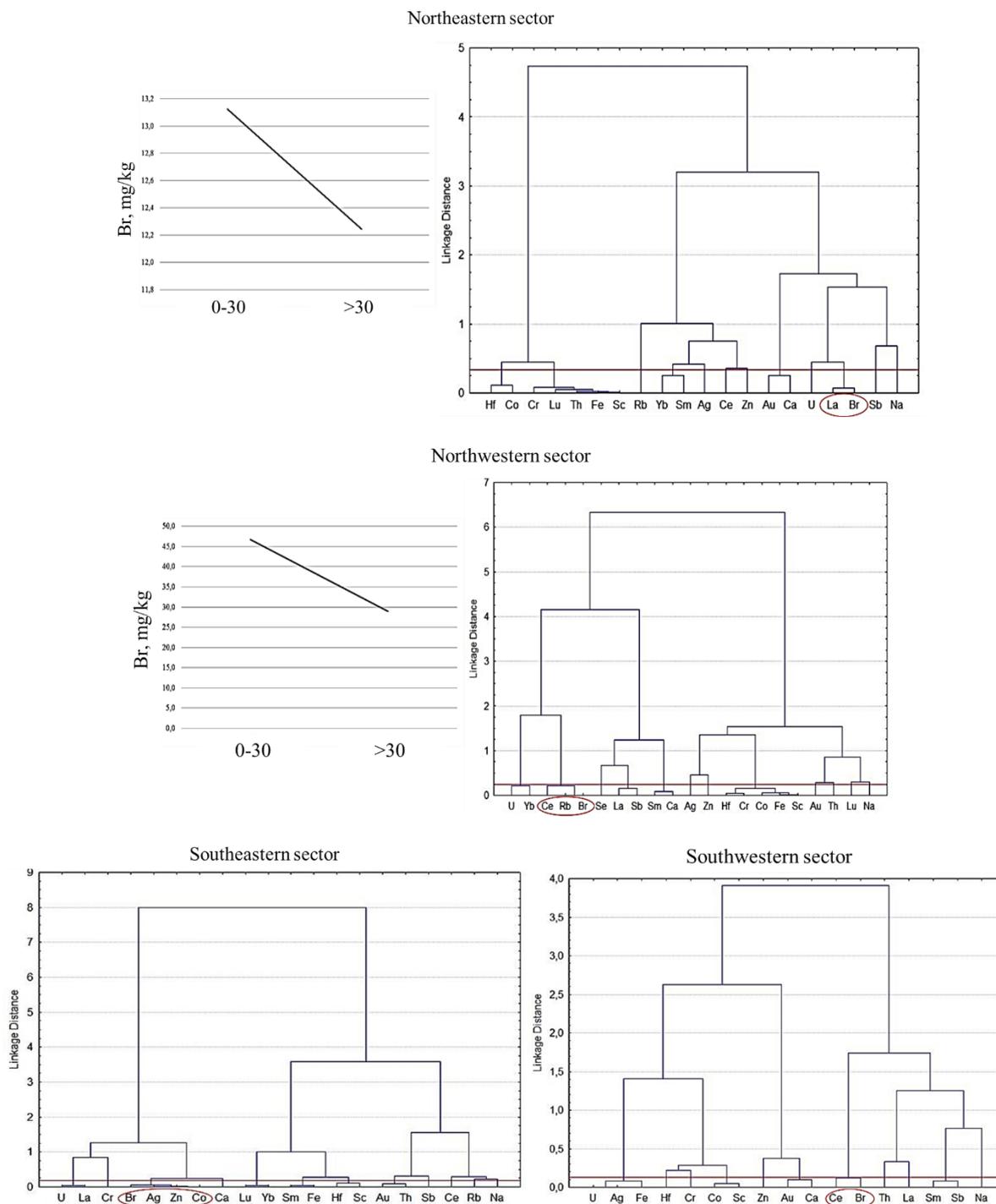


Figure 7.13 - Dendrograms of the correlation matrix of the geochemical spectrum of elements in children's hair by sectors of the Tomsky district and the change in bromine content (mg/kg) moving away from the industrial zone

In the northeastern direction, significant associations of bromine with lanthanum in the U-La group, associated with Sb-Na, are noted in the children's hair. In the northwest direction, significant bromine correlation is found in the Ce-Rb group, associated

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with U-Yb. We assume that the settlements of the north-eastern and north-western sectors are subject to complex natural and anthropogenic influences, including impacts from industrial enterprises - sources of bromine emissions into the environment, located within the Tomsk – Seversk industrial agglomeration.

It is worth paying special attention to the geochemical association of the element in the south-eastern and south-western sectors. If, in the south-western sector, the possible technogenic influence is still present, then in the southeastern sector new, previously not observed associations of the element (Ag-Zn-Co) are noted. Particularly noteworthy here is the significant correlation between bromine and silver. This metal is one of the most resistant to bromine, even at elevated temperatures and in the presence of moisture, whereas most metals hardly react with anhydrous bromine due to the formation of a protective bromide film on their surface. It is known that the its own minerals of bromine are very rare and are represented only by bromargyrite (AgBr), iodobromite ($2\text{AgCl} * 2\text{AgBr} * \text{AgJ}$) and embolite (Ag (Cl, Br)). Such correlation for bromine is noted not only in the hair of the inhabitants of this sector, but also in female organs and tissues from the Kaftanchikovo village, located in the same sector (*Baranovskaya et al., 2016*). Thus, this feature, which is already observed in two research objects, cannot be considered accidental, but rather natural, and conditioned by certain factors of this zone.

The results of changes in the bromine content over time, allow us to conclude that in recent years the halogen content in the children's hair of the Tomsky district has been reduced (Figure 7.14). At the same time, in the settlements located near the industrial zone, the concentration of the element has also decreased (Figure 7.15). This may be due to the fact that the reactors of the Siberian Chemical Combine, which are a potential source of bromine emissions into the environment (*Baranovskaya, Rikhvanov, 2002, Baranovskaya, 2003*), were stopped, and there was a change in the enterprise's operating mode. It could be also connected with the intensity of production at the petrochemical combine.

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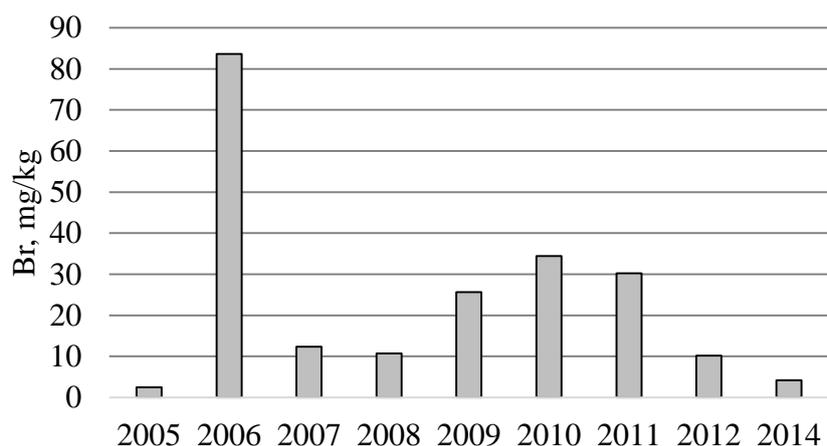
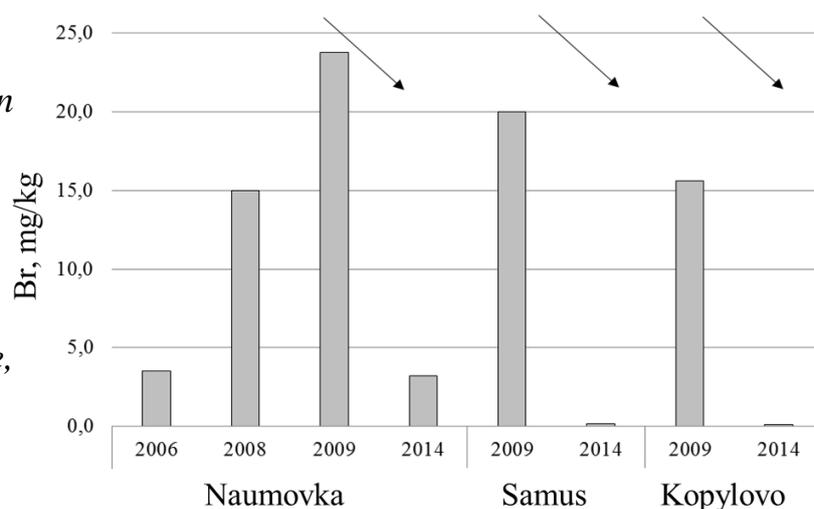


Figure 7.14 - Change in the content of bromine in the children's hair in the Tomsky district over the years, mg/kg

Figure 7.15 - Change in bromine content with years in the children's hair, living in the settlements, located near the industrial zone, mg/kg



Human blood. According to the statistical parameters of bromine distribution in the blood of residents of the Tomsky district, we can talk about its extremely uneven distribution. The variation coefficient, in the blood of residents is a maximum, at 153%, compared with other region's districts (Table 6.5). The analysis shows that the highest concentrations of the element are observed in this biosubstrate of Seversk city residents (Table 7.3), which was also noted by us for children's hair.

Table 7.3 – Concentration coefficient of bromine in blood of residents of the settlements of Tomsky district, relative to various indicators

Settlements	Concentration coefficient (relative to the average regional values)	Relative to the noosphere clarke (Glazovsky, 1982)	Relative to the clarke of sea water (Vinogradov, 1957)
Loskutovo	0,3	0,3	0,1
Kornilovo	0,4	0,4	0,1

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Samus	0,5	0,4	0,2
Kislovka	0,5	0,5	0,2
Kandinka	0,5	0,5	0,2
Tomsk	0,9	0,8	0,3
Naumovka	1,0	0,9	0,4
Chernaya rechka (Yuksa)	1,5	1,3	0,5
Seversk	5,8	5,2	2,0

In the blood of the residents of the Tomsky districts, we detected significant bromine correlations with Hf, Th, Ce and La (Fig. 7.16), which may indicate both the presence of natural geochemical anomalies (for example, zircon-ilmenite deposits) and anthropogenic impact. Thus, *Shatilov (2001)*, using the example of solid snow deposits, showed that these elements are specific to the heat and power industry and nuclear fuel cycle enterprises. Some bromine correlations are identical to those, found in the hair of residents, living in the north-east and north-west sectors of the district.

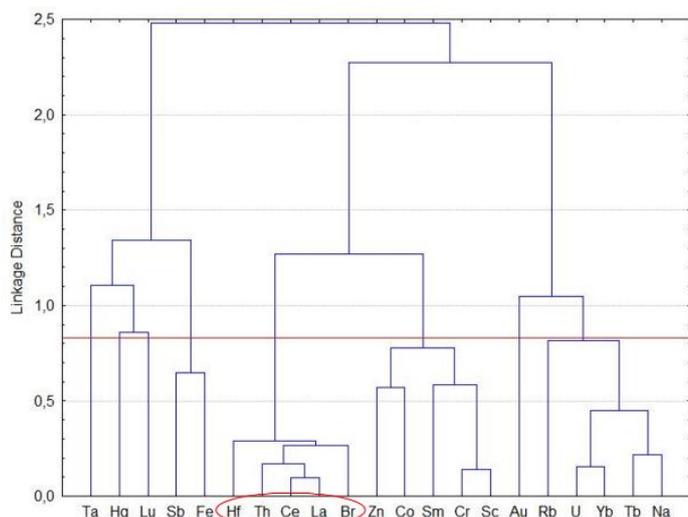


Figure 7.16 - Dendrogram of the correlation matrix of the geochemical spectrum of elements in the blood of the Tomsky district residents (1-Person $r(0.05) = 0.83$, sample size - 133 samples)

The analysis shows that, as for all the research objects we examined earlier, there is a tendency for in bromine in the blood of residents to decrease when we move further away from the Tomsk-Seversk industrial agglomeration (Figure 7.17).

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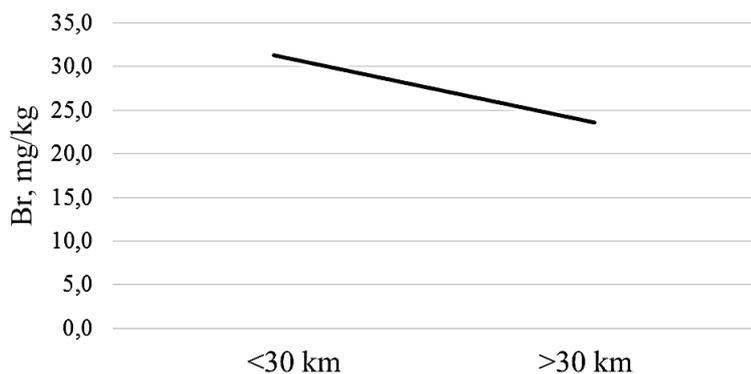


Figure 7.17 - The content of bromine in the blood of the residents when moving away from the industrial zone

Thyroid gland (pathologically altered tissue). Analysis of the actual material on the thyroid gland allows us to state that bromine is extremely heterogeneously distributed in the glands of the residents living in the Tomsky district. Whereas, if the maximum amounts of the element's accumulation in children's hair and blood were observed among the residents of Seversk city, for the thyroid gland, maximum concentrations of the element are observed among the population living in the villages of Zonal'naya Stantsiya and Samus (Figure 7.18). At the same time, in the thyroid gland, significant correlations of bromine are only found with cerium. In addition, there is a decrease in bromine in the biosubstrate with increasing distance from the Tomsk-Seversk industrial agglomeration.

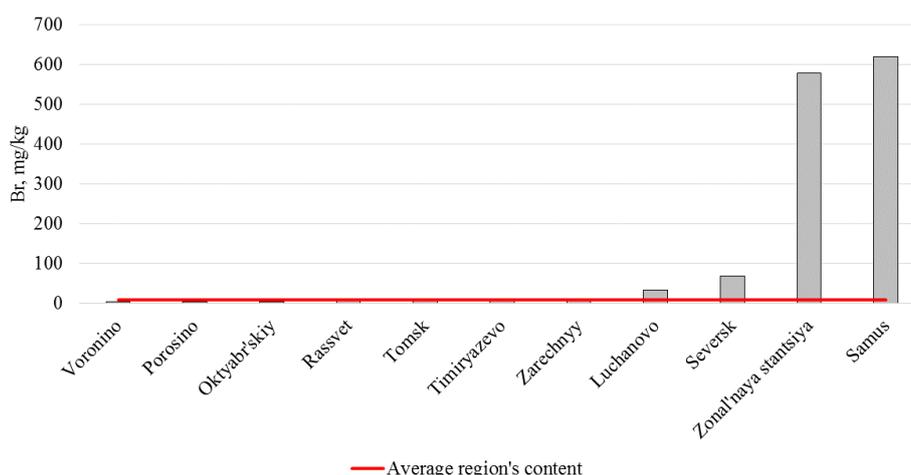


Figure 7.18 - Ranking of the settlements of Tomsky district according to the levels of accumulation of bromine (mg/kg) in pathologically altered thyroid glands of the residents

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Thus, the distribution of bromine in the human biosubstrates selected in the Tomsky district, is extremely heterogeneous. There is a general tendency towards decreasing element content when moving away from the zone of the Tomsk-Seversk industrial agglomeration. In the biomaterials, there are identical geochemical associations of the element with cerium and lanthanum. A comparative analysis of the study of bromine in children's hair over the years shows that there is a significant decrease in the content of the element both in the whole region and in its individual settlements.

Domestic pig organs. Based on the example of two piglets, selected in different sectors of the Tomsky district, we can clearly see the peculiarities of the accumulation of bromine, depending on the different degree of anthropogenic load. Thus, in the organs and tissues of a pig taken in the Kizhirovo settlement, located within the 30km zone of the Tomsk-Seversk industrial agglomeration in the north-west direction, we observed higher levels of bromine accumulation than in the pig taken from Verkhneye Sechenovo village, located at a distance of 38 km from the Tomsk-Seversk industrial agglomeration in the south-west direction (see Figure 6.11).

It should be noted that significant correlation of bromine with U and Na is observed in the organs and tissues of the pig of Kizhirovo village, and only with sodium in the pig from Verkhneye Sechenovo village. In addition, when studying the composition of the mineral phase of the tubular bone ash of domestic pigs (*Shakirova, 2013*) in two territories, the following feature was revealed: the presence of chlorine in the studied tissue of the Kizhirovo village domestic pig (Figure 7.19) and its absence in the tissue of the Verkhneye Sechenovo village pig (Figure 7.20). A similar pattern is noted for the underground waters of the Cretaceous deposits, where chloride ions are present in the Kizhirovo village zone, and absent from Verkhneye Sechenovo village (*Jankovic, 2017*).

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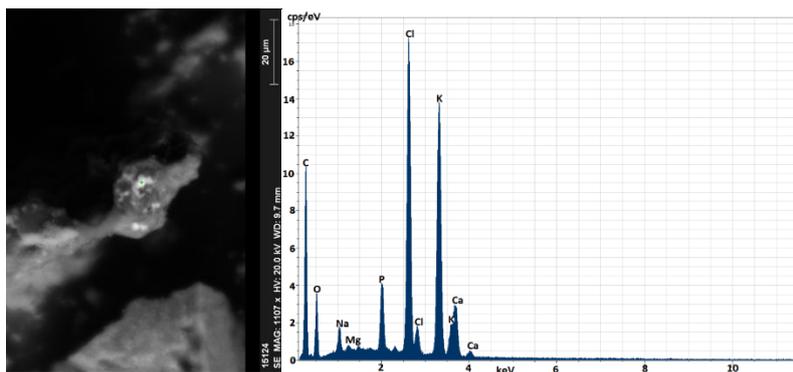


Figure 7.19 – The composition of the mineral phase of the tubular bone ash of a domestic pig (*Sus Scrofa Domestica*), Kizhirovo village; left - electron microscopy (zooming 15120); right –energy dispersive spectrum of chemical elements content in the sample

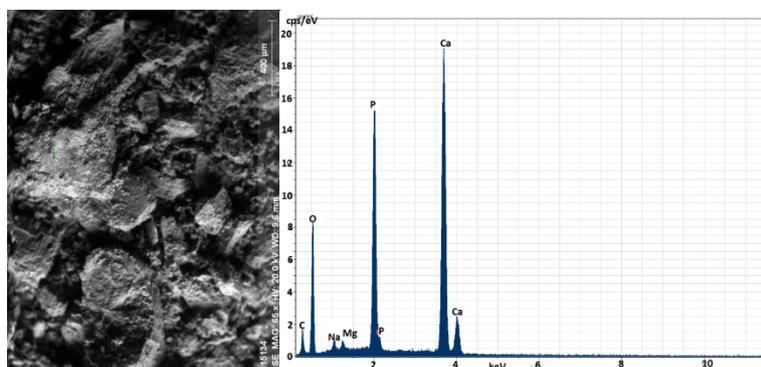


Figure 7.20. – The composition of the mineral phase of the tubular bone ash of a domestic pig (*Sus Scrofa Domestica*), Verhnesechenovo village; left - electron microscopy (zooming 15120); right –energy dispersive spectrum of chemical elements content in the sample

Thus, elevated bromine levels are observed in the organs and tissues of the piglet from the zone of technogenic influence of industrial enterprises of the Tomsky district, compared to those in the piglet organism selected in the opposite direction. In addition, in the organs and tissues of the first there is a significant presence of chlorine, close to the bromine chemical element, which is reflected in the spread of the chloride ion in the underground waters of the Cretaceous deposits.

All the trends for the material studied were generalized, the results obtained are presented in Table 7.4. It should be noted that for the environmental compartments we

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are studying, there is a general pattern, which consists in a decreasing bromine content when moving away from the zone of the Tomsk-Seversk industrial agglomeration. There are several settlements, located in the industrial zone, characterized by an increased content of the element relative to the average regional values. Thus, high levels of bromine accumulation are observed in soils, scale of drinking water and blood of the inhabitants of Naumovka village; in drinking water, scale of drinking water and children's hair of Kopylovo village; scale of drinking water, pigs' organs and tissues of Kizhirovo village; scale of drinking water and children's hair of Tomsk city, children's hair and blood of the inhabitants of Seversk city and of Chernaya Rechka village. Correlation analysis, carried out on research objects selected in different years, makes it possible to establish a possible change in the geochemical situation in soils and scale of drinking water in recent years, and its relative stability, characteristic of children's hair of the Tomsky district.

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Table 7.4 - Generalization of the analyzed data on the trend of bromine accumulation, geochemical associations of the element, as well as the identification of settlements in which the content of the element exceeds the average regional values

Research object	The tendency of Br accumulation moving away from the industrial zone (<30 km -> 30 km)					Settlements in which the bromine content exceeds the average regional values	Significant geochemical associations of bromine (based on the results of the coefficients of pair correlation)	
	general	sectors					till 2014	2014
		northeast	northwest	southeast	southwest			
Soils	–	–	–	–	–	Naumovka, Novoarkhangel'skoye	Sm, Tb	Sr
Bottom sediments	–	–	–	–	–	–	Sm, Lu, U, Yb, As, Na, La, Ce, Th, Cr, Hf, Ba, Ag, Cs, Sc, Tb, Rb, Fe, Ta, Co, Eu, Sb	
Drinking water	–	–	–	–	–	Kopylovo, Kuzovlevo	–	Cr
Drinking water scale	↘	↘	↘	↘	↗	Aleksandrovskoye, Barabinka, Vershinino, Voronino, Gubino, Dzerzhinskoye, Zarechnyy, Zonal'naya Stantsiya, Zorkal'tsevo, Kaltay, Kandinka, Kaftanchikovo, Kizhirovo, Kozyulino, Kopylovo, Kornilovo, Mazalovo, Mezheninovka, Molodezhnyy, Moryakovskiy Zaton, Naumovka, Novorozhdestvenskoye, Orlovka, Tomsk	Tb, Yb, Lu, Eu, Sm, La	Na, Fe, As, Cs, La, Eu, Hf, Th, U

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Children's hair	↘	↘	↘	-	-	Georgiyevka, Zonal'naya stantsiya, Kizhirovo , Kozyulino, Kopylovo , Moryakovskiy Zaton, Nelyubino, Orlovka, Polovinka, Rassvet, Samus, Seversk, Tomsk, Chernaya rechka (Yuksa)	La, Ce, Rb, Ag, Zn, Co	Na, Co, Ag, Sb, La , Hf Ca, Zn
Blood	↘	-	-	-	-	Naumovka, Seversk, Chernaya rechka (Yuksa)	Hf, Th, Ce, La	-
Thyroid gland	↘	-	-	-	-	Zonal'naya stantsiya, Samus	Ce	-
Organs and tissues of	↘	-	-	-	-	Kizhirovo	U, Na	-

Note: bold typestyle indicates settlements that are characterized by high levels of accumulation of the element in several study objects and identical geochemical associations of bromine with chemical elements observed in different years; red color denotes significant negative correlations of bromine.

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In addition, the analysis allows us to consider the balance of bromine distribution within the studied media in the settlements of the northwestern and northeastern sectors of the Tomsky district (Figure 7.21), due to their considerable technogenic transformation and high bromine intensity.

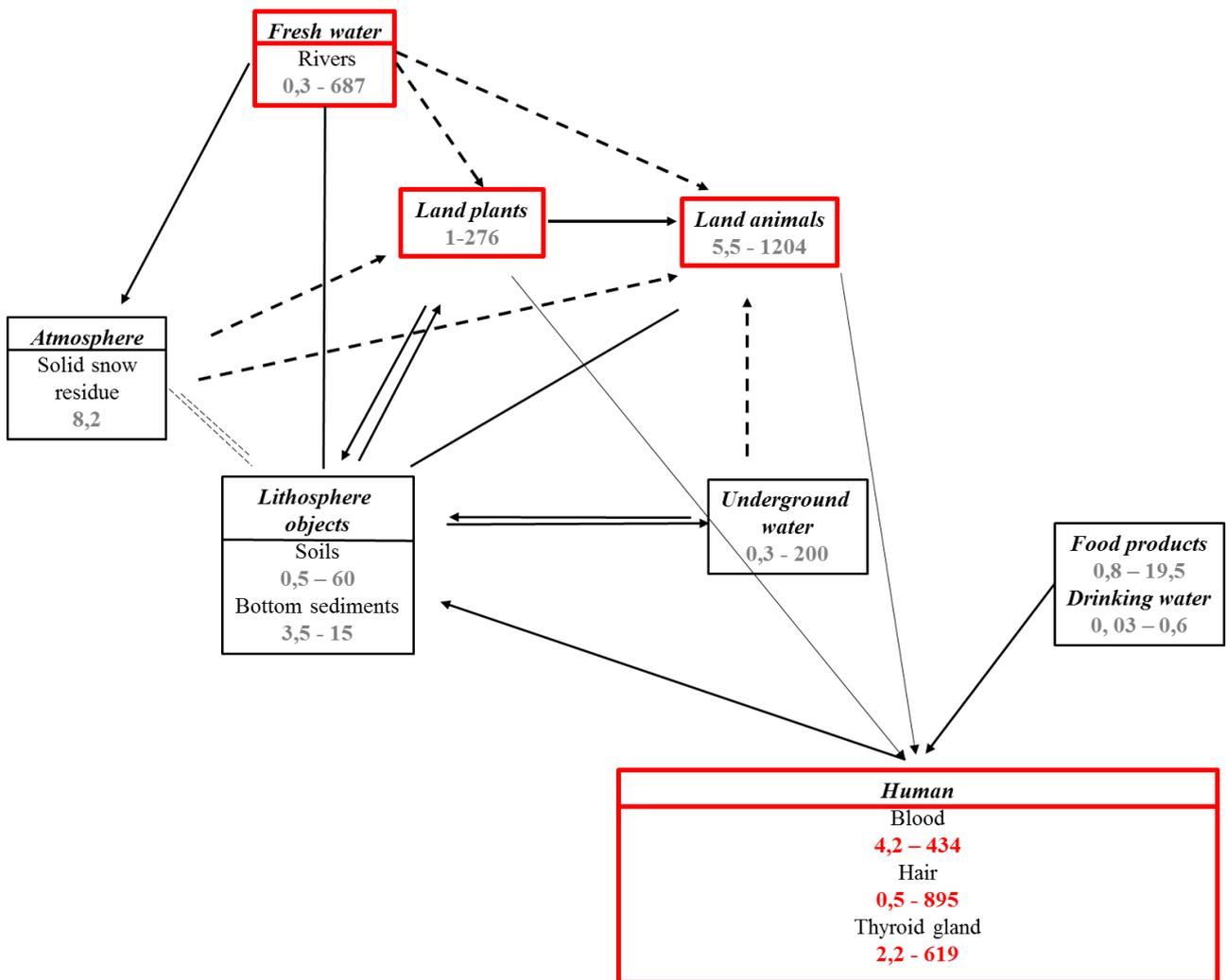


Figure 7.21 - Simplified scheme for the distribution of bromine in the environment of the Tomsky district (the Tomsk-Seversk industrial agglomeration) within the cycle of the element in nature, in mg/kg (for hydrosphere objects - in mg/l)

Note: data on fresh and underground waters is taken from Kolubaeva, 2015 (the range of minimum-maximum values in Tomsky district of the region is shown); snow solid sediment (industrial enterprises of Western Siberia) - according to Shatilov, 2001.

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Thus, it can be clearly seen that the maximum accumulation of bromine in living organisms of the Tomsk-Seversk industrial agglomeration occurs. Thus, it can be clearly seen that the maximum accumulation of bromine in living organisms occurs in the Tomsk-Seversk industrial agglomeration. There is a significant differentiation in the accumulation of the element in this zone compared to the literature sources and general data for the Tomsk region. Bromine content in the hair of children living near the industrial zone is more than 9 times higher than the content of the element in children of the Tomsky district (excluding this zone), and 12.5 times higher in the blood of residents. The content of bromine in the pathologically altered tissues of the thyroid gland of Tomsky district is characterized by much higher element concentrations than the data of the literature sources: they are 62 times higher. However, they are lower than the maximum accumulation levels observed in the thyroid gland in the Tomsk region, in general, due to abnormally high concentrations of the element in this biosubstrate of the inhabitants of the Shegarsky district. The content of bromine in the organs and tissues of terrestrial animals of the settlement within the industrial zone is 4 times higher than concentrations typical for the Tomsk region, and 4.5 times higher for terrestrial plants. In addition, increased element accumulation levels are also observed for the fresh waters of the region in comparison with data on the background territories.

7.3 Geochemical characteristics of natural environments in the areas located near oil refining enterprises

In view of the fact that bromine is a specific element of the petrochemical industry, in order to establish the geochemical specificity of natural environments near refinery facilities, we have studied the natural media and biomaterials selected in the locations of this type of enterprise. In 2014, drinking water, soil and poplar leaves were selected in the Grand Est region of France, where a large oil refinery is located. The same research objects, along with drinking water scale and children's hair were also selected, in the same year, in several settlements of the Tomsk-Seversk industrial zone, where the largest petrochemical plant in Russia, as well as a number of other diversified industrial enterprises are located. The analysis of the information obtained (according to ICP-MS

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data) shows that bromine is specifically and locally concentrated in the drinking waters of the studied territories (Table 7.5).

Table 7.5 - Geochemical series of chemical elements in drinking water in areas of location of oil refineries

Territory		Geochemical series of chemical elements
Settlements in Tomsky district	Samus	(Rb,In) _{1,8} Ba _{1,6} Sc _{1,4} (Na Cu) _{1,3} (Si,K,Sr) _{1,1}
	Naumovka	Mn _{3,7} B ₃ Pb _{2,6} Co _{2,4} Fe _{2,1} (Cu Zn) _{1,8} Cr _{1,2} (Ca Sc, Rb,Sb) _{1,1}
	Kuzovlevo	Sb _{1,5} Br _{1,4} Cu _{1,3} (Ca Zn) _{1,2} (Mg I) _{1,1}
	Zonal'naya stantsiya	Sb _{1,5} Co _{1,4} (Ca,Li,Ba) _{1,3} (Si,Sr) _{1,2} (B,Na,Mg,Cr) _{1,1}
	Kopylovo	U _{4,8} Mo _{3,7} Li _{2,3} K _{1,8} (Ti,Cs) _{1,7} Br _{1,4}
France	Grand-Est region	Al _{3,2} I _{2,6} Br _{2,3} B _{1,7} V _{1,5} (Be,U) _{1,4} (Na,Ti) _{1,3} Ce _{1,2} Fe _{1,1}

Note: Concentration coefficients were calculated relative to the sample average

So, in the territory of the Tomsky district in the zone of influence of the oil refinery combine "Sibur", bromine is found in the drinking waters of Kuzovlevo and Kopylovo settlements. The first of them is in close proximity to the main production facilities, and the second is a junction point for the transportation of petroleum products. We do not presume to judge the ways bromine enters the drinking waters nor how the spectra of the elements concentrated in them are obtained, but these preliminary results require further study in the future, both from the point of view of the natural factor of their formation and the technogenesis of the studied territory.

The complex nature of the territory, affected by the activities of the Tomsk-Seversk industrial agglomeration, is reflected in a very wide range of elements that are concentrated in poplar leaves (Table 7.6).

Table 7.6 - Geochemical series of chemical elements in poplar leaves in areas of location of oil refineries

Territory		Geochemical series of chemical elements
Settlements in Tomsky district	Samus	Sn ₅ Hg _{1,8} (B,Na,K) _{1,5} (Ge,Sr,Au,Pb) _{1,4} (Ba,W) _{1,3} (Mg,Co, Si,Sb) _{1,2}
	Naumovka	Be ₃ (Ni,Rb,Cd) ₂ Zn _{1,7} Ag _{1,6} (Sm,Eu) _{1,5} (Dy,Pr,Gd,Tb, Br) _{1,4} (Cu,As,Y) _{1,3} (Mn,Er,La,Ho,Nd, Yb) _{1,2} (Ca,Cr,Co, Se,Cs,Ba, Lu,Hg) _{1,1}

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	Kuzovlevo	(Ce,Tl) _{1,7} Be _{1,6} (Cd,Ge) _{1,5} Tm _{1,4} (Eu,Gd,Y,La,Pr,Nd,Tb, Ho,Er) _{1,3} (Mg,Sc,Ni,Co,Ba,Dy) _{1,2} (P,Ca,Mn,Sr,Sm, Yb) _{1,2}
	Zonal'naya stantsiya	Se _{2,2} Br_{1,9} V _{1,6} (Ti,Sb,Bi) _{1,5} W _{1,4} (Li,Zr,Pt,Th) _{1,3} (Cr,Nb,U) _{1,2} (Mg,Fe,Ga,As,Pb) _{1,1}
	Kopylovo	I ₄ Ta _{3,2} Mo _{2,9} Au _{2,6} (Al,Th) _{2,2} (Li,Hf) _{2,1} (Nb,V,Li,U) _{1,9} (Cs, Ti) _{1,8} (Ga,Zr) _{1,7} (Sc,Lu) _{1,5} Na _{1,4} P,Fe,Ce,Tb,Dy, Yb,Er, Hg,Pt,Pb) _{1,2} (Cr,Nd,Ho,Tm,Gd,As) _{1,1}
France	Grand-Est region	Br₂₂ Na _{19,7} Zr _{14,8} Au ₆ Se ₅ Sb ₄ I _{3,5} Ta _{3,2} V _{2,4} U _{2,3} (Nb,Hf) ₂ (Si,Ca) _{1,9} (Ti,P) _{1,6} Fe _{1,4} (As,Ag,Tl) _{1,3} (K,Zn,Pb) _{1,1}

Note: Concentration coefficients were calculated relative to the sample average

The Kopylovo settlement is characterized by the maximum spectrum of elements with above average accumulations in poplar leaves, with a bromine concentration coefficient equal to 0.2. In general, bromine does not belong to the elements typical of the trees in this area, while in France, in the area of the refinery, its concentrations are large and 5 times higher than the sample average value.

In the soils of settlements of the Tomsky district, bromine concentration coefficients exceeding 1 are noted only in the village Zonal'naya Stantsiya (Table 7.7), where, along with Naumovka, the maximum range of chemical elements is found. The accumulation of a considerable number of chemical elements is also characteristic of French soils, in which bromine accumulates above the average sample concentrations.

Table 7.7 - Geochemical series of chemical elements in soils in areas around oil refining complexes

Territory		Geochemical series of chemical elements
Settlements in Tomsky district	Samus	Ru _{1,8} (Ca,Si) _{1,2} (Se,Pb) _{1,1}
	Naumovka	(Cs,Li,V) _{1,5} (Cr,Fe,Ni,As) _{1,4} (Mg,I,Y,Ce,Pr,Nd,Sm,Eu, Gd,Tb,Dy, Ho,Er,Tm, Yb,Lu,W,Tl,Bi,Th,U) _{1,3} (Al,Co,Cu,Ga,Rb,Zr,Nb,Mo, La,Hf,Ta) _{1,2} (Ti,Sn,Ba) _{1,1}
	Zonal'naya stantsiya	Br_{1,9} (Na,I) _{1,4} Se _{1,3} (Mg,Ti,Mn,Co,Nb,La,Ce,Pr,Nd, Sm,Dy,Er, Yb, Ta,Th) _{1,2} (Al,V,Cr,Fe,Ga,Sr,Y, Zr,Sn,Eu,Gd,Tb,Ho,Lu,Hf,W) _{1,1} (B,Na,Mg,Cr) _{1,1}
	Kopylovo	(Zn,P) ₂ Ag _{1,9} (Mn,Sb) _{1,4} (Ca,Cu,Sn) _{1,3} Sr _{1,2} (Ti,Ge, Se,Nb,Mo,Ta) _{1,1}

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France	Grand-Est region	W _{5,7} I ₂ Hf _{1,8} (Ni,Zr) _{1,7} (Sn,La,Th) _{1,5} (Ce,Pb,U) _{1,4} (Ca,As, Se,Nb,Ag,Pr, Nd,Sm, Ta,Tl) _{1,3} (Cs, Br) _{1,2} (Li,Si,Ti,Rb,Y,Gd, Ho,Er,Tm, Yb,Lu) _{1,1}
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Note: Concentration coefficients were calculated relative to the sample average

The following two research objects are considered by us exclusively within the settlements of Tomsky district. Bromine has not been determined in the scale of drinking water, however, it is possible to trace in general terms the geochemical spectrum of elements that are typical for this object in this area (Table 7.8). It is noteworthy that in the scale of drinking water in one district, there are such wide differences in the accumulation of chemical elements.

Table 7.8 - Geochemical series of chemical elements in the scale of drinking water in areas of oil refineries

Territory		Geochemical series of chemical elements
Settlements in Tomsky district	Samus	(W,Lu,Ti) _{3,2} Mo _{3,1} Ag _{2,9} (Li,Rb) _{2,5} Al _{2,4} (Si,Ni,Nd) _{2,3} Zr _{2,1} Eu ₂ Na _{1,9} (Mg,Nb,Sn,Pb) _{1,8} (Cu,Sm) _{1,7} (Ba,Er,Yb) _{1,6} Tl _{1,3} (P,Ge,Pr) _{1,2} (K,Th) _{1,1}
	Naumovka	Mn _{2,5} Nb _{2,1} Fe _{1,6} Er _{1,3} Ge _{1,2} Yb _{1,1}
	Kuzovlevo	Zn _{3,9} Pb _{2,5} Cu _{1,6} Cd _{1,3} Ge _{1,2} (Mg,Co) _{1,1}
	Zonal'naya stantsiya	Sr _{2,1} Ba ₂ Ag _{1,6} Ge _{1,5} Cu _{1,4}
	Kopylovo	U _{3,4} Cs _{3,3} (Sb,Cd) _{2,6} Se _{1,9} (Ni,Bi) _{1,7} Ga _{1,4} Nd _{1,3} (Sr,Th) _{1,2} (Ca,As) _{1,1}

Note: Concentration coefficients were calculated relative to the sample average

A different picture is observed when studying geochemical specificity in the example of the hair of children living in the zone of influence of the petrochemical combine (Table 7.9). In this zone, bromine is observed in the settlements of Samus and Kopylovo villages. In the latter, bromine also accumulates in drinking water.

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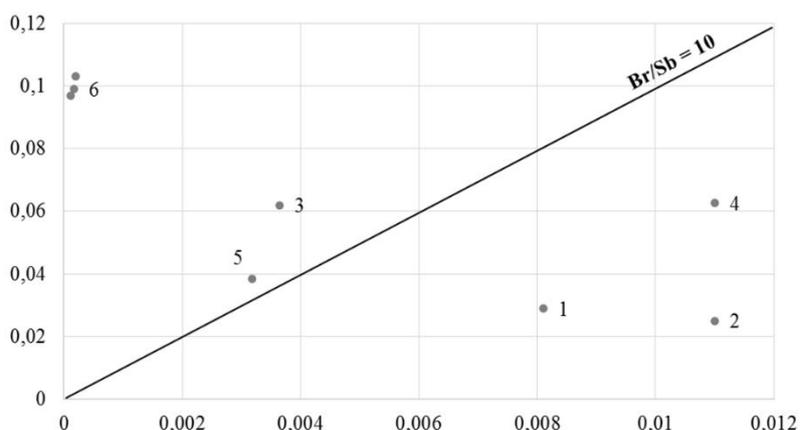
Table 7.9 - Geochemical series of chemical elements in the children's hair in the areas of location of oil refining complexes

Territory	Geochemical series of chemical elements
Settlements in Tomsky district	Samus (Na,La) _{1,6} (Sc,Hg, Br) _{1,4} (V,Ce,Ag) _{1,5} (Sb,Li,Rb,K, Tl,As,Cd) _{1,3} (Mn,Ba,Pb) _{1,2} (Co,Zn,Ge,Sr,Sm,Tb,Dy) _{1,1}
	Naumovka Pt _{2,1} Ni _{1,7} (Cr,I) _{1,6} Yb _{1,5} (P,Mo) _{1,4} (Si,Ta) _{1,3} (K,Rb,Nb, Lu) _{1,2} (Mg,Ti,Fe,Sn,Cs,Eu,Bi) _{1,1}
	Kuzovlevo (Sm,Au) _{1,7} I _{1,5} (Cd,Ba,Nd,Gd) _{1,4} (Al,Se) _{1,3} (Mg,Ca,Cu, Zn,Sr,Nb, Sn,Pr,Dy,Ho,Pb,Th,Hf,Ta) _{1,2} (Co,Cs,Eu,W, Hg) _{1,1}
	Zonal'naya stantsiya Ge _{2,9} Li _{2,7} Ca _{2,1} As _{1,8} Eu _{1,6} Fe _{1,5} (Al,Mg,Sc,Co,La,Ho) _{1,4} (Ga,Sr,Zr) _{1,3} (Si,Ti,Mn,Cs,Ce,Gd,Lu,Bi) _{1,2} (Cu,Pr, Nd,Pt,Th) _{1,1}
	Kopylovo U ₉ (Au,Hf _{2,1})Se ₂ (Sn,Ag,Zr) _{1,7} Br _{1,6} Pb _{1,5} (Na,As) _{1,3} Lu _{1,2} (V,I,Ta) _{1,1}

Note: Concentration coefficients were calculated relative to the sample average

The study of geochemical indicators in the form of ratios of chemical elements is of great importance (Rikhvanov, 1997; Yazikov, 2006). For example, the specific indicator used to determine air pollution from transport exhaust gases is the Br/Pb ratio, which is theoretically calculated to be 0.386, the so-called ethyl ratio (Saet et al., 1990). We also examined some new ratios of bromine with chemical elements (see Table 7.10).

According to a number of studies (Shatilov, 2001, Yazikov, 2006, Baranovskaya, 2011, etc.), antimony and bromine are elements specific to the petrochemical industry, which served as a starting point for considering the Br/Sb ratio in natural environments and biomaterials in the areas of oil refining complexes (7.22).



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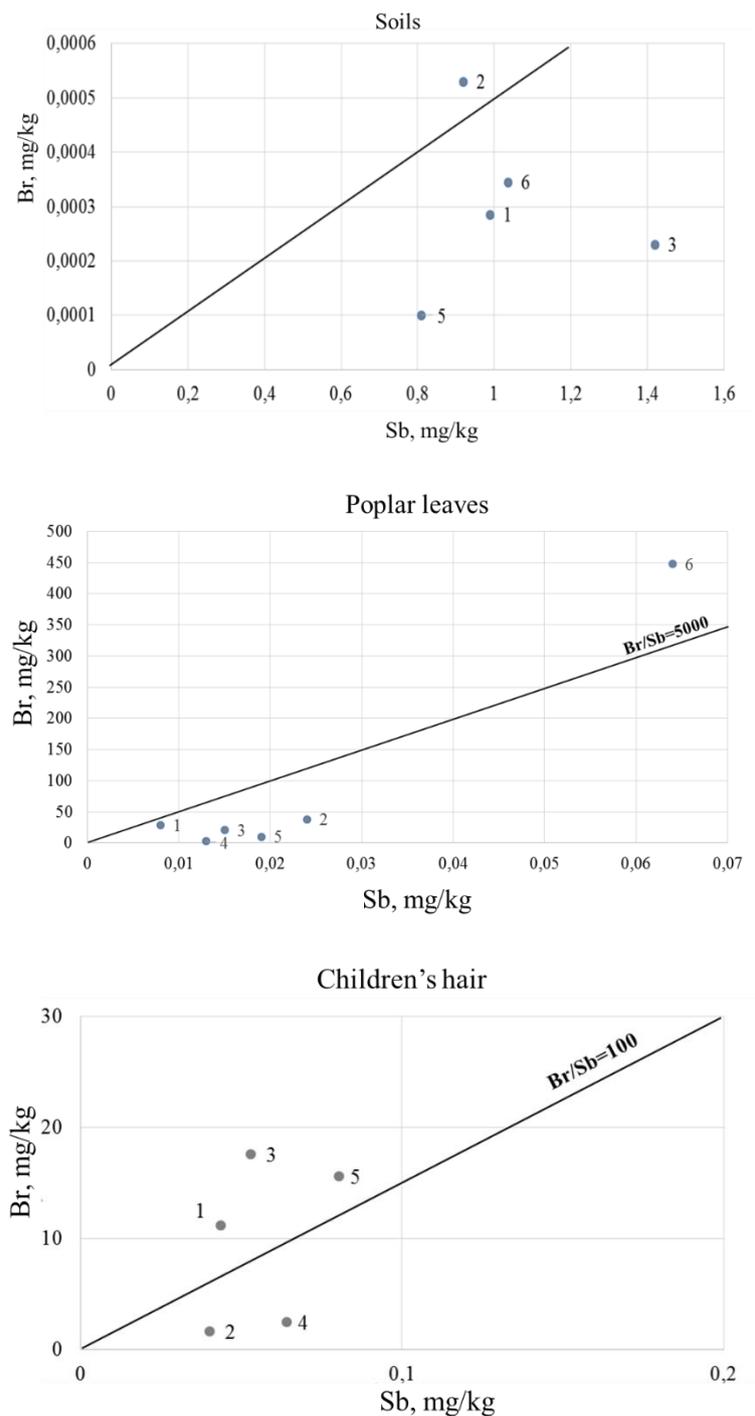


Figure 7.22 - *Br/Sb ratios in natural media and biomaterials around oil refining complexes*

Note: 1 - Naumovka, 2 - Zonal'naya stantsiya, 3 - Kopylovo, 4 - Kuzovlevo, 5 - Samus, 6 – France

A summary of the considered indicators of bromine with other chemical elements in natural media and biomaterials is presented in Table 7.10.

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Table 7.10 - Indicators of the ratio of bromine with chemical elements in natural environments in the areas of oil refining complexes

Territory		Ratios																			
		Na/Br				Br/Sb				Br/Pb				Br/U				Br/I			
		Drinking water	Soils	Poplar leaves	Children's hair	Drinking water	Soils	Poplar leaves	Children's hair	Drinking water	Soils	Poplar leaves	Children's hair	Drinking water	Soils	Poplar leaves	Children's hair	Drinking water	Soils	Poplar leaves	Children's hair
Settlements in Tomsky district	Samus	531	9*10 ⁴	2,3	50	12	0,0001	542	195	14	4*10 ⁻⁶	29	4	770	0,0001	3029	6308	2	5	1030	325
	Naumovka	362	3*10 ⁴	0,2	28	4	0,0003	3588	257	4	2*10 ⁻⁵	205	8	578	0,0002	12478	5185	5	4	28700	55
	Kuzovlevo	241	–	4,3	83	6	–	254	38	23	–	17	1	1252	–	1065	232	5	–	330	13
	Zonal'naya stantsiya	734	3*10 ⁴	0,4	101	2	0,0006	1592	42	47	3*10 ⁻⁵	136	1	500	0,0003	6702	234	3	7	2388	15
	Kopylovo	250	4*10 ⁴	1,1	37	17	0,0003	1407	332	126	1*10 ⁻⁵	68	3	15	0,0002	2453	80	9	6	117	129
France	Grand-Est region	193	3*10 ⁴	0,7	–	866	0,0003	7000	–	485	4*10 ⁻⁶	1600	–	92	0,0002	43077	–	4	3	2800	–
		201				576				495				76				4			
		220				518				515				82				3			

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As the analysis of Figure 7.22 and Table 7.10 shows, the Br/Sb ratio in drinking water of two settlements of the Tomsky districts: Kopylovo and Samus villages is greater than 10. In terms of this ratio in soils, Naumovka and Kopylovo villages are highlighted. In these villages the Br/Sb ratio is equal to 0.0003, which is also the case for the soils in France. Differences in this ratio are clearly recorded in the study of poplar leaves, where the settlements of the Tomsk region are grouped when the ratio is changed from 254 to 3588, while for the territory of France it is 7000. As for the changing of this ratio in children's hair there is a group of settlements – Naumovka, Kopylovo and Samus, where the ratio of bromine – antimony is more than 100.

In drinking water, very similar Na/Br ratios are obtained in the settlements Kuzovlevo and Kopylovo, as well as the studied territory in France. According to this ratio, the highest values of Na/Br ratio are in the soils of Samus village. In drinking water and poplar leaves, the highest Br/Pb ratio is typical for the studied territory of France, and the smallest for the village Naumovka. However, the latter shows the highest bromine - lead ratio in the hair of children living in this village. For drinking water in settlements of the Tomsky district, the Br/U ratio is more than 500, with the exception of the Kopylovo settlement. This ratio is relatively stable in the soils of all areas studied, but it varies greatly in poplar leaves. The Br/I ratio in drinking water is highest in Kopylovo village. However, the poplar leaves here show the lowest ratio. Regarding children's hair, the settlements of Samus and Kopylovo can be identified with the highest values of the bromine - iodine ratio.

Brief conclusion

Thus, using the example of studied media in the area around/ near to the petrochemical combine in France, high levels of bromine accumulation are clearly observed. This is also manifested when studying the indicator indices of the ratio of bromine with other chemical elements in different media. This indicates that bromine is a chemical element specific to this production. On the territory of Tomsky district this specificity is more difficult to identify, which may be due to the complex natural and technogenic character

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of the territory, influenced by the numerous enterprises of the Tomsk-Seversk industrial agglomeration. This is also reflected in the increased concentrations of a wide range of chemical elements and the instability of their indicator ratios with bromine.

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**CHAPTER 8. ESTIMATION OF THE TOXIC IMPACT OF
BROMINE ON ECOSYSTEMS AND HUMAN HEALTH BY
ECOLOGICAL MODELING**

The high toxicity of bromine along with its negative impact on living organisms dictate the need for a careful study of the toxic effect of the element on the quality of ecosystems and human health. To achieve this goal, we chose the USEtox environmental model, the advantages of which were discussed in detail in Chapter 3 of this paper, and the main methodological aspects in Chapter 4.

Despite the availability of information on a wide range of chemicals in the model database (the USEtox allows the toxicity calculation of more than 3000 organic compounds and 25 inorganic metal elements), bromine is not included in it. Based on joint work with the authors of the model, we were able to integrate the element and study its potential toxic effects within the framework of the USEtox 2.02 version and the corresponding methodological guidelines. It should be emphasized that only non-carcinogenic toxic effects of bromine were considered since necessary data on the carcinogenicity of the element is not available.

The initial data for obtaining the toxicity characterization factors for bromine (registration number CAS 7726-95-6) in environmental components are presented in Table 8.1.

Table 8.1 - Initial data used to calculate the toxicity characterization factors for Br

Parameter, unit	Value	Reference
Molar mass, g/mol ⁴	159,81	<i>Mendeleev's Periodic Table</i>
Partitioning coefficient between octanol and water, l/l	10,72	<i>US Environmental..., 2010</i>
Solubility (at 25°C), mg/l	17110	<i>Gandolli, 1999</i>
Vapour pressure (at 25°C), Pa	28700	<i>Lide, 1993</i>
Partitioning coefficient between suspended solids and water, l/kg ⁵	5,5E+01	<i>Handbook of Parameter Values, 2010</i>
Partitioning coefficient between sediment particles and water, l/kg ²	5,5E+01	
Partitioning coefficient between soil particles and water, l/kg ²	5,5E+01	<i>Handbook of Parameter Values, 2010</i>
Rate constant degradation in air, 1/s	1,7E-02	<i>Fan, 1992</i>

⁴ A molecule of bromine is diatomic; the molar mass taken into account was thus for Br₂.

⁵ According to IAEA, 2009 (Appendix A-2), organic carbon does not play a major role in partitioning for metals and the same partitioning is assumed, regardless of the soil, suspended sediment or bottom sediment phase.

Rate constant degradation in water, 1/s	1,0E-20	<i>USEtox 2.02</i>
Rate constant degradation in sediments, 1/s	1,0E-20	
Rate constant degradation in soils, 1/s	1,0E-20	
Bioaccumulation factor in plant roots, kg _{veg} /kg _{soil} ⁶	3,00E-01	<i>Human health risk assessment ... , 2005</i>
Bioaccumulation factor in plant leaves, kg _{veg} /kg _{soil}	1,50E+00	
Biotransfer factor in meat, d/kg _{meat}	2,50E-02	
Biotransfer factor in milk, d/kg _{milk}	2,00E-02	
Bioaccumulation factor in fish, 1/kg _{fish}	1,60E+02	<i>Kennedy, 1992</i>
Average of the log-values of the species-specific averaged ecotoxicity EC ₅₀	-0.27	One trophic level, <i>Daphnia magna</i> , was taken into account, the calculation was carried out according to the formula 3.8 based on <i>Human health risk assessment ... , 2005</i>
Human-equivalent lifetime dose per person that causes a non-cancerous disease probability of 50% after inhalation	5,80E-02	The calculation was carried out according to formula 3.7 based on <i>ECHA, 2017</i>
Human-equivalent lifetime dose per person that causes a non-cancerous disease probability of 50% after ingestion	3,93E+00	The calculation was carried out according to the formula 3.6 based on <i>Bromine – general information ... , 2009</i>

The calculated toxicity characterization factors for bromine for human and ecosystems (see formula 4.4) are presented in Figures 8.1 and 8.1a, respectively. These factors are represented by default, i.e. showing general results that do not take into account territorial differences.

As can be seen from the figures, characterization factors are not the same in various environmental components. The element is most dangerous for ecosystems in fresh water, and is the least dangerous in seawater, with identical effect in soils, regardless of their type. In contrast to the toxicity of bromine for ecosystems, the element is most

⁶ Converted from dry weight to wet weight by dividing by a factor of 5

Chapter 8. Estimation of the toxic impact of bromine on ecosystems and human health by ecological modeling dangerous for humans in soils used for agricultural purposes. The element can also have a toxic effect on human health via the air. Among all studied environmental components, bromine in natural soils and sea water has the least effect on humans.

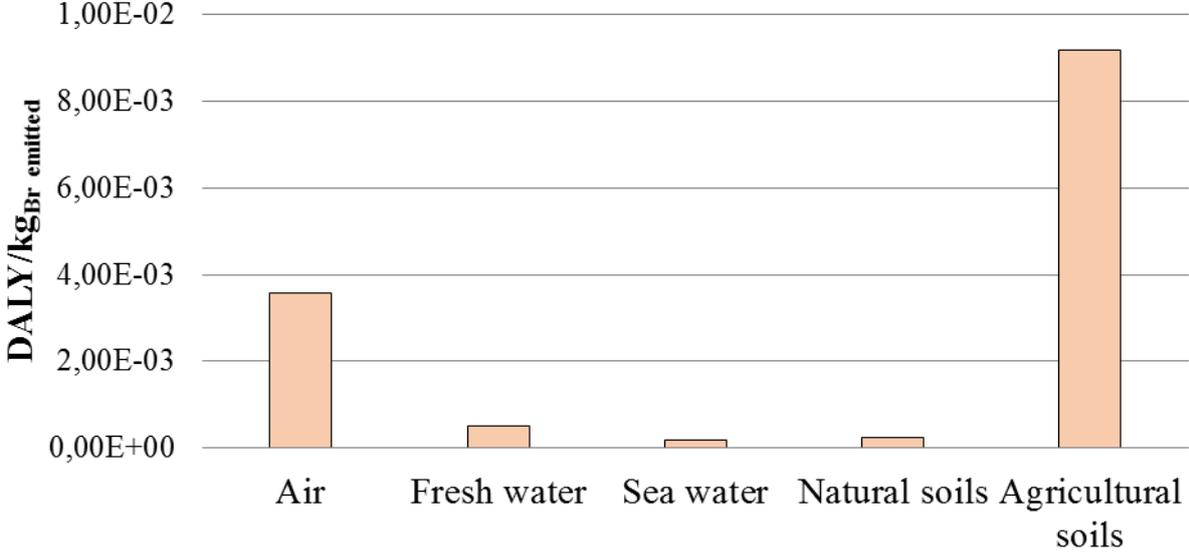


Figure 8.1 - Toxicity characterization factors for bromine for human health, $DALY/kgBr_{emitted}$

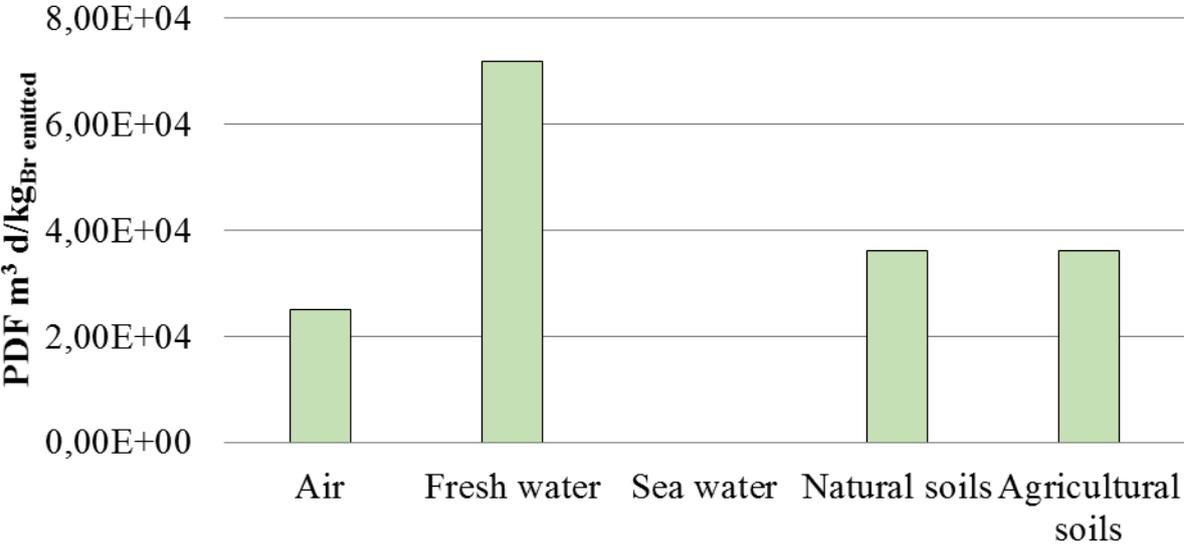


Figure 8.1a - Toxicity characterization factors for bromine for ecosystems, $PDF m^3 d/kgBr_{emitted}$

In general, it can be concluded that the results obtained in the framework of modeling do not contradict information in the literature. So, according to the modeling,

Chapter 8. Estimation of the toxic impact of bromine on ecosystems and human health by ecological modeling

in the sea water the element is effectively not dangerous for ecosystems, which, in our opinion, is logical, since marine organisms are able to accumulate elevated element concentrations without any effects. On the basis of these results, the same conclusion can be reached on the toxicity of bromine for human health. The high toxic effect associated with agricultural soils can be associated with the use of various fumigants, since the impact caused by inhalation is widely known and is reflected in regulatory documents.

A comparative analysis on the characterization factors, available in the model and the results we obtained, was done in order to evaluate the contribution of bromine to the toxicity indicators among all chemical elements included. As the results show, among 19 elements (*Ag(I)*, *As(III)*, *As(V)*, *Ba(II)*, *Be(II)*, *Cd(II)*, *Cr(III)*, *Cr(VI)*, *Cu(II)*, *Hg(II)*, *Mo(VI)*, *Ni(II)*, *Pb(II)*, *Sb(III)*, *Sb(V)*, *Tl(I)*, *V(V)*, *Zn(II)*), bromine's contribution to human health indicators ranges from 0.0001% to 0.32%. However, bromine's contribution to ecotoxicity indicator, while comparing it with 27 other elements (*Ag(I)*, *Al(III)*, *As(III)*, *As(V)*, *Ba(II)*, *Be(II)*, *Cd(II)*, *Co(II)*, *Cr(III)*, *Cr(VI)*, *Cs(I)*, *Cu(II)*, *Fe(II)*, *Fe(III)*, *Hg(II)*, *Mn(II)*, *Mo(VI)*, *Ni(II)*, *Pb(II)*, *Sb(III)*, *Sb(V)*, *Se(IV)*, *Sn(II)*, *Sr(II)*, *Tl(I)*, *V(V)*, *Zn(II)*), changes from 0.35% to 17.28%. This is clearly reflected in Figure 8.1b. Thus, we can conclude that the bromine's contribution to the human health toxicity indicator is higher than for the ecotoxicity one.

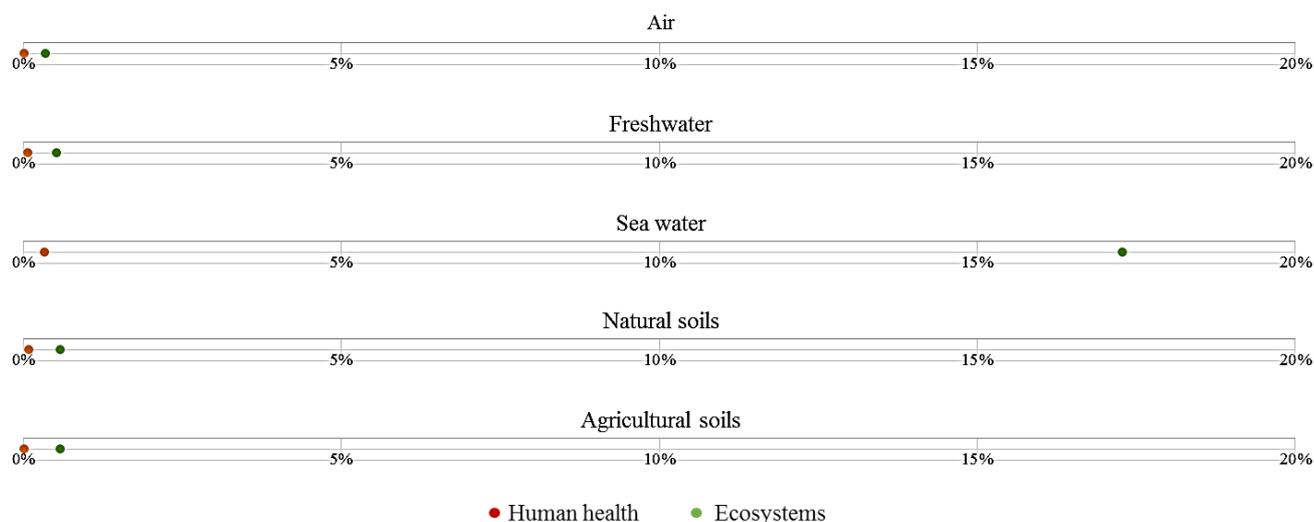


Figure 8.1b – Bromine's contribution to toxicity indicators (in %)

**8.1 Application of a model for assessing the toxicity and ecotoxicity of bromine in
the environment of different landscapes and geographical zones**

As already noted, the distinctive feature of this model is the inclusion of geographical differentiation of the territory. The model divides the whole territory of the globe into 8 continental or 17 subcontinental zones (Appendix B), each of which is characterized by specific climatic, hydrological indicators, population size, food consumption, etc. (Kounina et al., 2014). Accordingly, the values of the toxicity characterization factors for humans and ecosystems in different geographical areas may vary widely.

In the context of this work, we also examined the Tomsk region with the characteristic features of its territory. All the initial data for the Tomsk region, integrated into the model, are presented in Table 8.2.

Table 8.2 - Parameters used to calculate toxicity characterization factors for the territory of the Tomsk region

Parameter	Value	Reference	
Area land, km ²	3,14E+05	<i>Basic social and economic characteristics ... , 2017</i>	
Area sea, km ²	1,37E+04	<i>Calculated in the model</i>	
Area fraction _{natural soil} [-]	9,37E-01	<i>Basic social and economic characteristics ... , 2017</i>	
Area fraction _{agricultural soil} [-]	4,40E-02		
Average annual temperature, °C	9,00E-01	<i>Weather and climate , 2017</i>	
Surface wind speed, m/s	1,60E+00		
Average annual rainfall, mm/year	5,68E+02	<i>Weather and climate , 2017</i>	
Soil erosion, mm/year	3,00E-02	USEtox 2.02	
Watering of the territory, km ³	4,19E+00	Calculated in the model	
Total population	1,08E+06	Basic social and economic characteristics ... , 2017	
The number of urban population (on average)	1,83E+05		
Producti on-based intake rates	Above-ground produce, kg/(day*capita)	3,62E-01	<i>Consumption of basic food products ... , 2017</i>
	Below-ground produce, kg/(day*capita)	6,77E-01	

	Meat, kg/(day*capita), kg/(day*capita)	1,67E-01	<i>Basic social and economic characteristics ..., 2017</i>
	Dairy products, kg/(day*capita)	7,10E-01	
	Fish freshwater, kg/(day*capita)	3,07E-03	
	Fish coastal marine water, kg/(day*capita)	4,60E-02	

The results obtained in Figures 8.3 and 8.4⁷ demonstrate the complete heterogeneity of the toxic effect of bromine in various physico-geographical conditions.

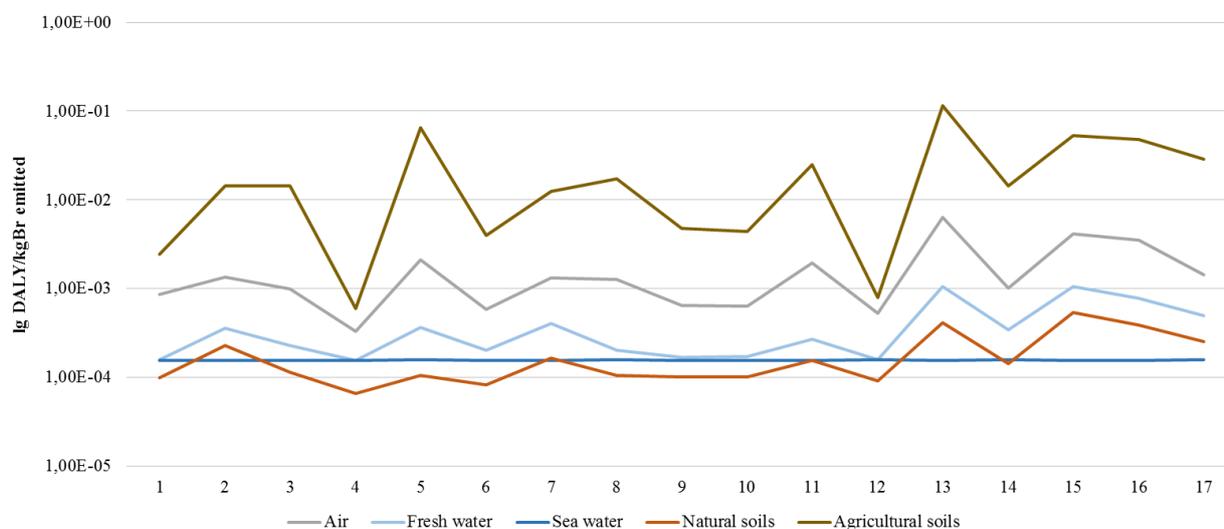


Figure 8.3 - Toxicity bromine characterization factors for humans in different geographic and landscape areas, $DALY/kgBr_{emitted}$

The greatest risk to human health due to the toxic effects of bromine in the air, fresh water, natural and agricultural soils is manifested within South Australia and New Zealand, Europe, India, and Eastern China. The lowest impact is observed in Northern Australia, as well as in Northern Europe and Canada, due primarily to significant differences in the population of these areas, as well as climatic characteristics (wind speed, rainfall, etc.). It can also be noted that, in general, the Tomsk region does not

⁷ Note: 1 - Tomsk region, 2 - Central Asia, 3 - Indochina, 4 - Northern Australia, 5 - South Australia and New Zealand, 6 - South Africa, 7 - North, South, West and Central Africa, 8 - Argentina + 9 - Brazil +, 10 - Central America and the Caribbean, 11 - USA and South Canada, 12 - Northern Europe and Northern Canada, 13 - Europe, 14 - East India and the Pacific, 15 - India, 16 - Eastern China, 17 - Japan and the Korean Peninsula.

The list of territories included in each zone is detailed in Appendix A.

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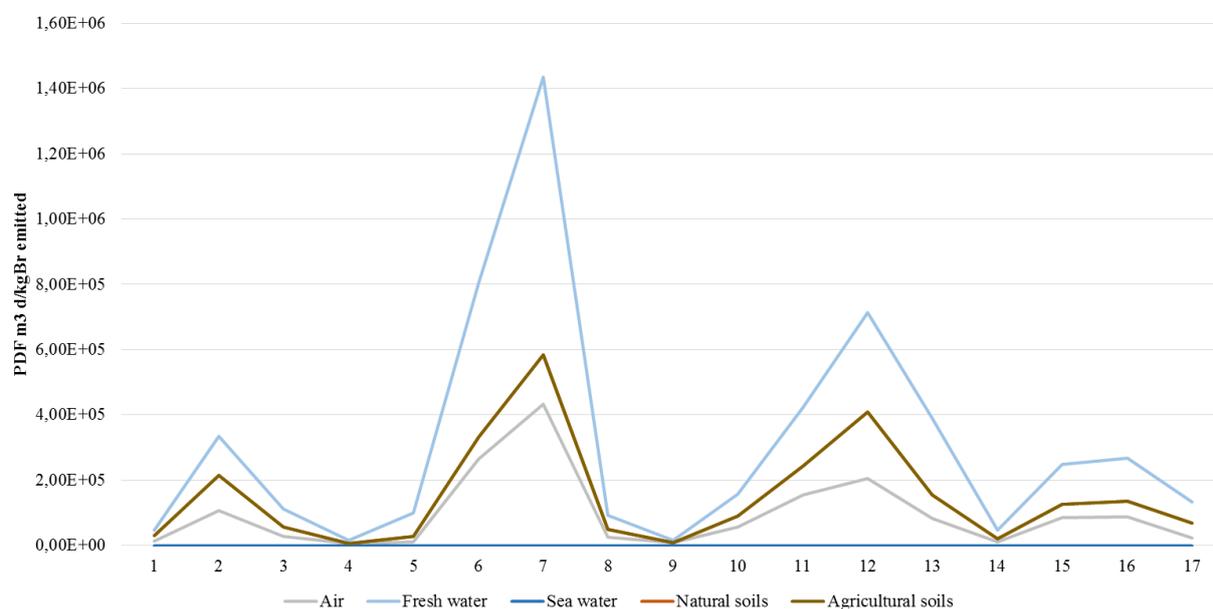


Figure 8.4 - Toxicity bromine characterization factors for ecosystems in different geographic and landscape areas, PDF m3 d/kgBr emitted

A completely different picture is observed when considering the toxicity of bromine for ecosystems within different geographical zones. Then the greatest risk is noted in all studied environmental objects, except for sea water, in North, South, West and Central Africa. Increased risk is also observed in the US, Southern and Northern Canada and Europe. The risk for ecosystems in the Tomsk region can be described as one of the lowest one, along with North Australia, Brazil, the East Indies and the Pacific.

8.2 Application of the model for assessing the toxicity and ecotoxicity of bromine in soils of the Tomsk region

Among the environmental components presented, we paid more attention to the soil. Soil, being a biocosm body, represents a unique combination of biotic and abiotic components and is one of the most important environmental media (*Ecological and geochemical features ...*, 2006). It is characterized by the presence of complex processes, under the influence of which there is constant transport and transformation of chemicals, many of which can be toxic and potentially dangerous. Being itself a major

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acceptor of pollutants, soil can also be a source of secondary pollution of the atmosphere, surface and groundwater, and living organisms (*Ecological and geochemical ...*, 2006).

In addition to exceptional cases of direct soil consumption (geophagia, accidental ingestion by children or poor food washing) (*Nyanza et al.*, 2014), the main pathways of chemical pollutants from soils to humans are trophic chains. Soil is a main source of nutrients for plants, which, in turn, are consumed by higher organisms including domestic animals and humans. Thus, the chemical compounds entering the human body through food chains originate from soils (*Brevik et al.*, 2015). A significant amount of work is devoted to the role of soil as one of the factors contributing to the occurrence of diseases (*Rikhvanov et al.*, 1993; *Abrahams*, 2001; *Brevik et al.*, 2015). This, undoubtedly, dictates the need for a thorough study of its chemical composition.

A number of specific features of the Tomsk region (increased watershed in the northern and central parts of the region, the strong influence of the relief on soil formation, carbonate depletion within the middle taiga and enrichment in the southern, harsh climate) contribute to the formation of a diverse soil cover over its territory. The soils of the region are mainly sod-podzolic and peaty-marsh, and in the southern part - gray forest. Chernozems occupy the best drained areas of the south of the Ob river. The soils of the region are characterized by an increased hydromorphism, a large part of the soil cover is characterized by low natural fertility, soils contain little humus (*Evseeva*, 2001).

The total land area of the Tomsk region is 31439.1 hectares, with most of the territory represented by forests - about 85%. Agricultural land represents over 8%, including arable land with about 2.1% of the territory (*Fusella*, 2013). The quality of land in the region is low, the most productive lands are located along the river valleys and in the southern part of the region, where agricultural land development ranges from 18 to 45%, compared with less than 1% in the northern regions (*Evseeva*, 2001). The main agricultural areas include Kozhevnikovsky, Shegarsky, Krivosheinsky, Teguldetsky, Molchanovsky, Bakcharsky, Tomsky, Asinovsky and Zyryansky districts. It should be noted that little research has been done on the soils of the Tomsk region in

Chapter 8. Estimation of the toxic impact of bromine on ecosystems and human health by ecological modeling terms of bromine (*Perminova et al., 2017*), and there is no information on its effect on living organisms through soil cover.

Using the example of soils in the Tomsk region, we will clearly demonstrate the possible use of the model to determine the toxic effects on ecosystems and human health, as well as the grading of areas of the region in terms of the degree of danger. The results of the quantitative determination of bromine in the soils of the Tomsk region by the INAA method, along with the calculated toxicity bromine characterization factors for ecosystems and humans within the Tomsk region considered by us in the previous section, served as the basis for calculating the toxicity impact score (see formula 4.3). It is worth noting that we considered the complex entry of the element: both through inhalation and oral (via food, i.e. agricultural crops) from the soil cover to living organisms.

It should be emphasized that soils used for agricultural purposes (in household plots of settlements) were selected in all districts of the region, while in the Tomsky district, natural soils near industrial plants were selected. In addition, the results of INAA, presented in mg/kg, were recalculated in kg according to formula 4.9. The general toxicity impact scores on ecosystems and human health are presented in Table 8.3.

Table 8.3 - Toxicity impact scores for humans and ecosystems within the Tomsk region

№	District	Concentration of Br in soils, mg/kg (according to the INAA results)	Toxicity impact score	
			for humans, CTU_{hum}	for ecosystems, CTU_{eco}
3	Parabelsky	14.8	74.53	9.3×10^5
4	Kolpashevsky	11.9	59.93	7.5×10^5
5	Chainsky	15.3	77.05	9.6×10^5
6	Molchanovsky	14.5	73.02	9.1×10^5
7	Krivosheinsky	16.8	84.61	1.1×10^6
8	Shegarsky	14.3	72.02	9.0×10^5
9	Kozhevnikovsky	29,8	150,08	1.9×10^6
10	Tomsky	9.3	41.01	1.2×10^7
11	Asinovsky	19.7	99.21	1.2×10^6
12	Pervomaysky	15.6	78.56	9.8×10^5
13	Verkhneketsky	13.6	68.49	8.5×10^5

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14	Teguldetsky	13.2	66.48	8.3×10^5
15	Zyriansky	10.8	54.39	6.8×10^5
16	Bakcharsky	39.4	198.42	2.5×10^6
17	Tomsk region (average)	14.6	73.53	9.1×10^5

For better clarity, the results of the total toxicity impact score of bromine in Table 8.3 are also shown in Figures 8.5 and 8.6.

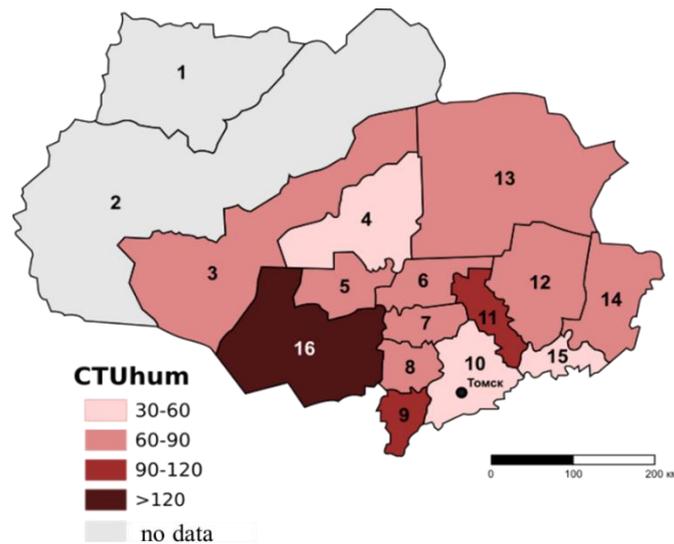


Figure 8.5 - Total toxicity impact score of toxic effects of bromine on human health, CTUhum

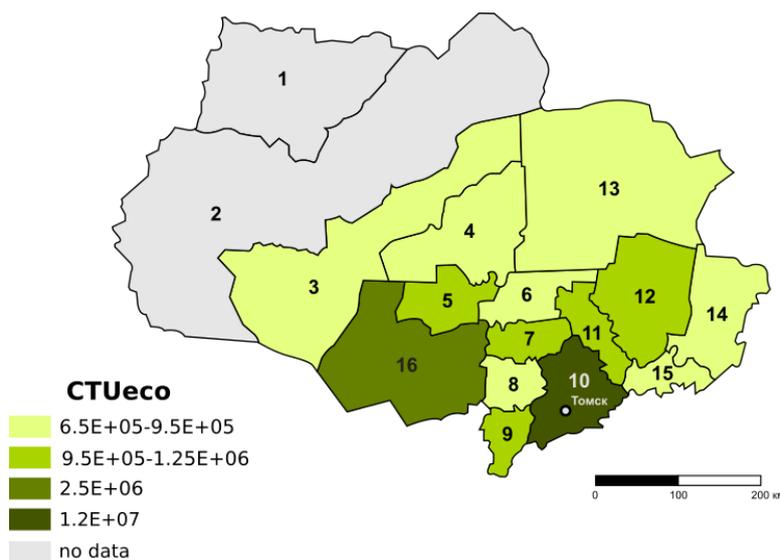


Figure 8.6 - Total toxicity impact score of toxic effects of bromine on ecosystems, CTUeco

As figure 8.5 shows, the minimal toxic effect of bromine on human health, due to the content of the element in the soils, is observed in the Kolpashevsky, the Zyryansky and the Tomsky districts. This is, first of all, due to low concentrations of the halogen in soils. In addition, the low risk noted in the Tomsky district is related to the fact of selection of natural soils, rather than agricultural, as in other districts of the region. An increased risk to human health is noted in the Kozhevnikovsky and the Asinovsky districts, and the highest one - in the Bakcharsky one, where maximum levels of bromine accumulation in soil are noted.

Figure 8.6 demonstrates that the toxic effect of bromine on ecosystems is significantly different from its effect on human health. The minimum risk for ecosystems, due to the content of the element in the soils, is observed in a number of districts of the region: Parabelsky, Kolpashevsky, Molchanovsky, Shegarsky, Verkhneketsky, Teguldetsky and Zyryansky. In the Bakcharsky district, where there is a maximum risk to human health, the risk to ecosystems is not the greatest. In addition, an completely opposite picture is typical for the Tomsky district, where the risk to human health is minimal, but maximal for ecosystems.

Despite the fact that, considering a single element we are able to identify areas by the degree of risk to ecosystems and humans, identifying the least and the riskiest of them, we cannot judge the danger that bromine could, present due to the absence of any standards or scales in the USEtox model. In order to understand whether the toxic effects of bromine represent a serious hazard, we also considered other chemical elements, total toxicity impact scores that were calculated similarly to those for bromine.

We compared the chemical elements available in the USEtox model database (25 metals) with elements determined by the INAA method (26 elements). Thus, 5 elements are available: Cr, As, Ag, Sb and Ba to compare the total toxicity impact score of bromine to human health. For ecosystems 9 elements: Cr, Fe, Co, As, Sr, Ag, Sb, Cs, Ba, were considered. The total toxicity impact scores of bromine (in %), on human health and ecosystems are presented in Figures 8.7 and 8.8 respectively⁸.

⁸ 3-16 - districts of the Tomsk region, as in Table 8.3; 17 - average for the Tomsk region.

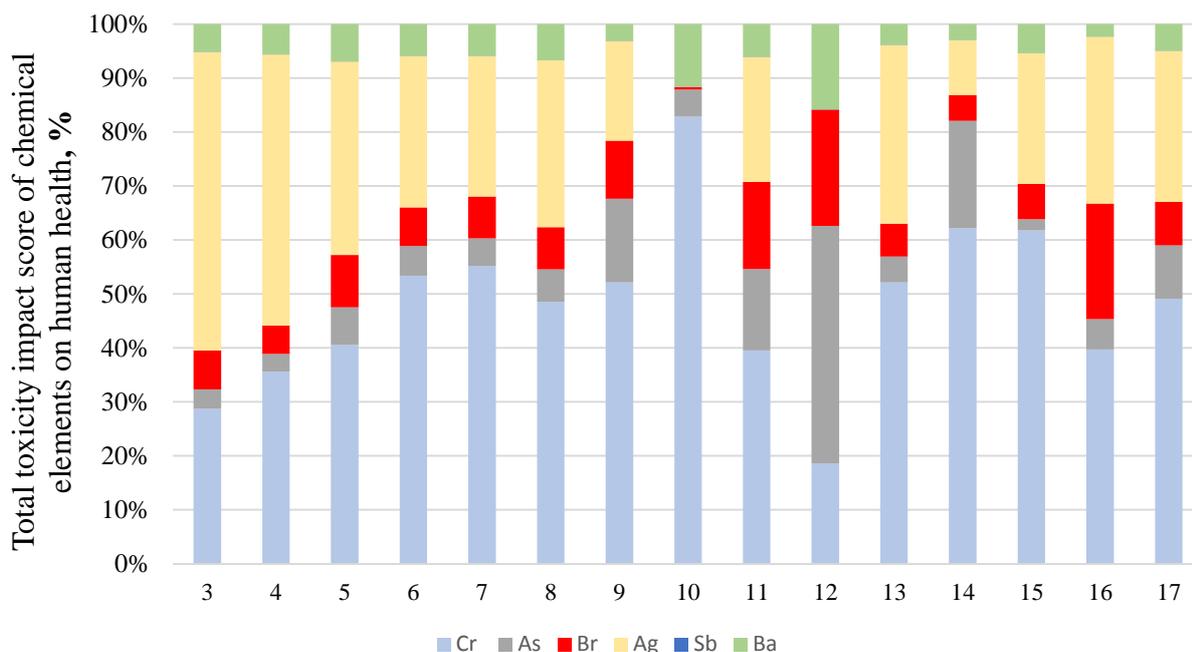


Figure 8.7 - Total toxicity impact score (%) of chemical elements on human health

As can be seen from Figure 8.7, the greatest contribution to toxic effects on human health is not made by bromine, but mainly by silver, chromium and arsenic. The detailed contribution of each individual element to the total toxicity impact scores is presented in Table 8.4.

Table 8.4 - Contribution of chemical elements to the total toxicity impact score on human health

Districts	The contribution of elements to the total toxicity impact score on human health					
	Br	Cr	As	Ag	Sb	Ba
Parabelsky	7,2%	28,7%	3,6%	55,3%	0,004%	5,2%
Kolpashevsky	5,3%	35,6%	3,3%	50,2%	0,006%	5,6%
Chainsky	9,7%	40,5%	7,0%	35,9%	0,009%	6,9%
Molchanovsky	7,2%	53,4%	5,5%	28,1%	0,008%	5,9%
Krivosheinsky	7,7%	55,2%	5,1%	26,1%	0,004%	5,8%
Shegarsky	7,8%	48,5%	6,0%	31,0%	0,008%	6,7%
Kozhevnikovsky	10,8%	52,1%	15,5%	18,5%	0,006%	3,1%
Tomsky	0,5%	82,8%	5,0%	0,0%	0,016%	11,6%
Asinovsky	16,1%	39,6%	15,1%	23,2%	0,015%	6,0%
Pervomaysky	21,6%	18,6%	44,0%	0,0%	0,029%	15,8%
Verkhneketsky	6,1%	52,1%	4,8%	33,1%	0,003%	3,8%
Teguldetsky	4,7%	62,2%	19,9%	10,2%	0,006%	3,0%

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Zyriansky	6,6%	61,8%	2,0%	24,2%	0,008%	5,4%
Bakcharsky	21,4%	39,7%	5,6%	30,9%	0,006%	2,3%

Chromium is the main element, whose contribution to total toxicity impact score is the highest in comparison with other elements, and ranges from 39.6% to 82.8% in various districts of the region. The greatest contribution to the toxic effects on human health in the Parabelsky and the Kolpashevsky districts is made by silver. In the Pervomaisky district, the highest toxicity is due to high levels of arsenic in soils.

The toxic effect of bromine on human health within different districts of the region varies from 0.5% to 21.6%. In general, it can be concluded that the toxic effect of bromine on human health relative to other chemical elements is not high. It is noteworthy that in the Bakcharsky district, where the maximum levels of bromine accumulation are found in soils, the element's contribution to the total toxicity impact score is not dominant.

When studying the toxic effect of bromine on ecosystems, it was found that iron is the main element contributing to the total toxicity impact score, ranging from 69.4% to 91.8% in different districts, which is due to high levels of its accumulation in the soils of the Tomsk region. In view of this fact, we calculated the total toxicity impact score of chemical elements on ecosystems without taking into iron account, for a more objective assessment (Figure 8.8).

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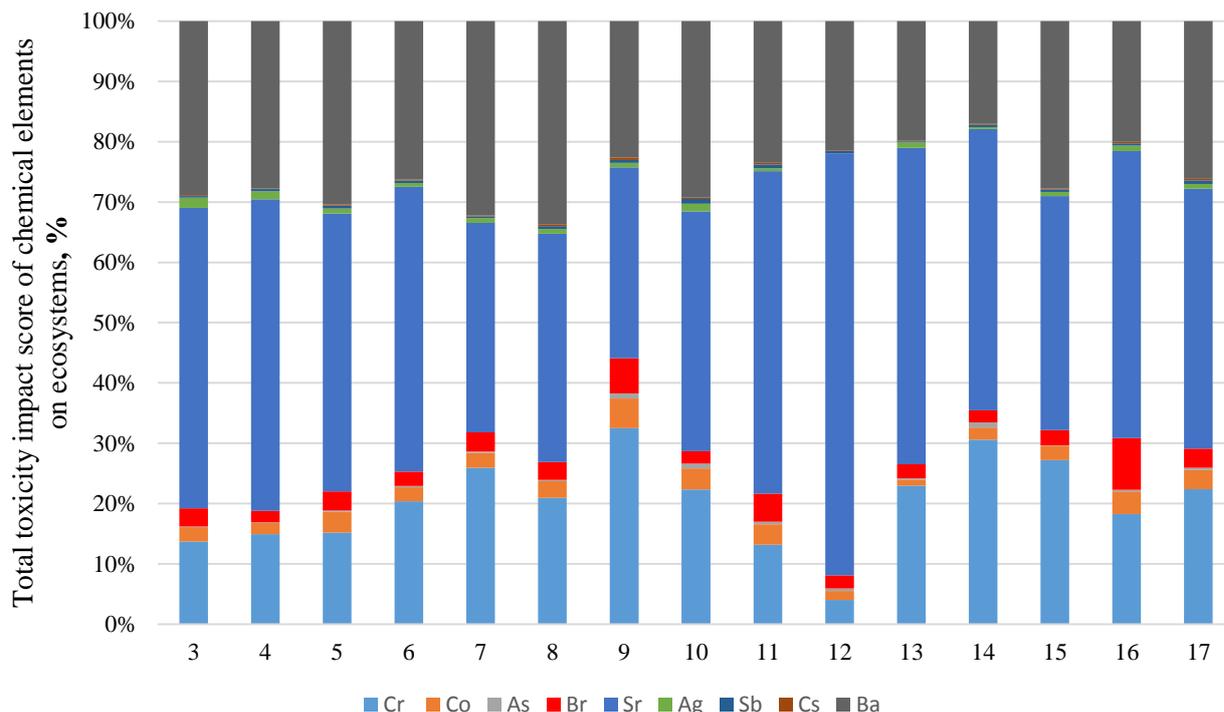


Figure 8.8 - Total toxicity impact score (%) of chemical elements on ecosystems

As can be seen from the above figure, bromine is not the element that plays a primary role in the total toxicity impact score on ecosystems. Other elements that contribute to the total toxicity impact score are strontium, chromium and barium. The contribution of individual elements to the total toxicity impact score for ecosystems is presented in Table 8.5.

Table 8.5 - Contribution of chemical elements to the total toxicity impact score on ecosystems

Districts	The contribution of elements to the total toxicity impact score on ecosystems								
	Br	Sr	Cr	Co	As	Ag	Sb	Cs	Ba
Parabelsky	3,0%	49,8%	13,7%	2,4%	0,1%	1,7%	0,3%	0,2%	28,9%
Kolpashevsky	1,9%	51,7%	14,9%	1,8%	0,1%	1,3%	0,4%	0,1%	27,7%
Chainsky	3,2%	46,1%	15,2%	3,4%	0,2%	0,8%	0,4%	0,2%	30,4%
Molchanovsky	2,4%	47,2%	20,4%	2,4%	0,2%	0,7%	0,4%	0,2%	26,3%
Krivosheinsky	3,2%	34,8%	26,0%	2,5%	0,2%	0,8%	0,3%	0,2%	32,3%
Shegarsky	2,9%	37,8%	20,9%	2,8%	0,2%	0,8%	0,4%	0,3%	33,7%
Kozhevnikovsky	5,9%	31,7%	32,5%	4,9%	0,8%	0,7%	0,5%	0,4%	22,6%
Tomsky	2,1%	39,7%	22,4%	3,5%	0,8%	1,3%	0,8%	0,3%	29,3%
Asinovsky	4,7%	53,5%	13,2%	3,4%	0,4%	0,5%	0,6%	0,3%	23,5%
Pervomaysky	2,2%	70,0%	4,0%	1,5%	0,4%	0,0%	0,4%	0,1%	21,4%

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Verkhneketsky	2,3%	52,5%	23,0%	1,0%	0,2%	0,9%	0,2%	0,1%	19,8%
Teguldetsky	2,0%	46,7%	30,6%	2,0%	0,8%	0,3%	0,4%	0,2%	17,0%
Zyriansky	2,5%	38,8%	27,2%	2,3%	0,1%	0,7%	0,4%	0,2%	27,7%
Bakcharsky	8,6%	47,6%	18,2%	3,8%	0,2%	0,9%	0,4%	0,3%	20,0%

The greatest contribution to the total ecotoxicity impact score is made by strontium, ranging from 31.7% to 70.0% in different districts. The second element that contributes to toxic effects on ecosystems is barium, whose share in total ecotoxicity is 17.0% - 33.7%. The third element is chromium, its value in the total ecotoxicity impact score varies from 4% to 32.5%. The contribution of bromine varies from 1.9% to 8.6%, thereby determining its fourth place in the total ecotoxicity impact score among the chemical elements studied. The average contribution of cobalt, silver, antimony, arsenic and cesium is 2.7%, 0.8%, 0.4%, 0.3% and 0.2%, respectively.

As can be seen from Table 8.5, the most toxic bromine contents for ecosystems are in the soils of the Bakcharsky and the Kozhevnikovsky districts. The remaining districts of the region are characterized by relative homogeneity in terms of the risk due to toxic effects of bromine. The proportion of bromine in the total ecotoxicity impact score can be characterized as an average. The element makes relatively little contribution to it, however, according to the results of the modeling it is more dangerous for ecosystems than, for example, cobalt, silver, antimony, arsenic and cesium.

8.2.1 Assessment of the relationship between the toxicity of bromine in soils and the level of morbidity in the population of the Tomsk region

There is a very little known about the relationship between bromine in the environment and the health of the population of the Tomsk region. *O.A. Denisova (2011)* showed the relationship between bromine levels in the pathologically altered thyroid gland and the incidence of diffuse non-toxic goiter. However, there is no data on the relationship between bromine in the soils of the Tomsk region and the health of the inhabitants of this territory. Thus, in the framework of this study, we attempted for the first time to eliminate this gap by analyzing the results on the toxicity of bromine in soil cover, presented in the previous section (Figure 8.5), with available data on the incidence of diseases of the population of the Tomsk region. For this information, state reports

"On the state of sanitary and epidemiological welfare of the population in the Tomsk region", carried out in the period 2006-2015, were used.

The results of soil studies of the Tomsk region on sanitary-toxicological, bacteriological and parasitological indicators show that of the 659 investigated soils, about ten percent do not meet hygienic standards for the maintenance of sanitary-indicative microorganisms: 8.5% - according to the bacterial index of the E. coli group; 3.9% - the index of enterococci. Out of 647 investigated soils, there are 0.5% cases of helminths eggs (Aleksandrovsky district, Tomsky district). Assessment of the degree of epidemiological danger of soil cover shows that 79.1% of the study areas of the Tomsk region are clean; 12.2% are moderately hazardous; 6.1% - dangerous, and 2.6% - extremely dangerous (*State report ..., 2013*).

Analysis of medical and biological health indicators of the population of the Tomsk region shows that during the period from 2007 to 2011 the general morbidity of the population was at the level of 1577.6 ± 17.5 (per 1000 population) (*State report ..., 2013*). At the same time, the level of general morbidity of residents is higher than in the Siberian Federal District as a whole. Significant contributions to the level of the general morbidity of the population of the Tomsk region are made by diseases of the respiratory system and circulatory system, malignant neoplasms, diseases of the digestive and respiratory organs, as well as infectious and parasitic diseases (*State report ..., 2016*).

Within the region, abnormally high levels of total mortality were observed in seven districts (Figure 8.9), and of infant mortality in eight (Figure 8.10).



Figure 8.9 – Territory at "risk" of the general mortality of the population (State report ..., 2016).

Figure 8.10 – Territory at "risk" of infant mortality (State report 1 ..., 2016).



Note for figures 8.9 and 8.10: green – does not exceed the Tomsk region levels; yellow – exceeds the Tomsk region levels by 1,1-1,4 times; pink - exceeds the Tomsk region levels by 1,5 times or more

According to the Federal Information of Social and Hygienic Monitoring during 2012 to 2014, the Tomsk region is included in the "risk" group for mortality of the population from malignant formations⁹ (Figure 8.11):

- breast cancer - 12.9%;
- skin - 11.6%

⁹ Percentage shows incidence rate

- respiratory organs - 10,6% (the highest mortality rates are observed in the Verkhneketsky, Krivosheinsky, Parabelsky, Tomsky and Chainsky districts);
- thyroid gland (1.1 times in excess of the level of the Russian Federation, in Bakcharsky, Tomsky districts and Tomsk city, death rates 1.3-1.5 times higher than in the Tomsk region);
- stomach - 6.7% (*State report..., 2012, 2016*).



Figure 8.11 - Territory at "risk" of mortality of the population from malignant formations (*State report..., 2016*).

Note: green – does not exceed the Tomsk region levels; yellow – exceeds the Tomsk region levels by 1,1-1,4 times; pink - exceeds the Tomsk region levels by 1,5 times or more

The incidence of stomach and duodenum ulcers in the Tomsk region by age categories in 2014 was at the following levels: children (0-14 years) - 19.4% (per 1000), adolescents (15-17 years) - 91.9%₀₀₀, adults (18 years and over) - 105.6%₀₀₀ (The state sanitary and epidemiological ..., 2016). Spatial analysis of stomach and duodenum ulcer diseases in children, adolescents and adults is shown in Figure 8.12 (a, b, c, respectively).



Figure 8.12 - Territories at "risk" of the incidence of gastric ulcer and duodenal ulcer among: a - children (0-14 years), b - adolescents (15-17 years), c - adults (figure done by the author on the basis of data "The state sanitary and epidemiological ..., 2016"). Note: green –does not exceed the Tomsk region levels; pink - exceeds the Tomsk region levels

The primary incidence of gastritis and duodenitis was at the following levels in 2014: children (0-14 years) -1368.3 per 100 thousand of the population of the corresponding age group, adolescents (15-17 years) - 1705.1% , adults (18 years and older) - 394.5% (State report..., 2016). Spatial analysis of the incidence of gastritis and duodenitis among children, adolescents and adults is shown in Figure 8.13 (a, b, c, respectively).



Figure 8.13 - Territory at the "risk" of the incidence of gastritis and duodenitis among: a - children (0-14 years), b - adolescents (15-17 years), c - adults (the figure done by the author on the basis of data "The state sanitary and epidemiological ..., 2016"). Note: green - does not exceed the Tomsk region levels; yellow – exceeds the Tomsk region levels by 1,1-1,4 times; pink - exceed the Tomsk region levels by 1,5 times or more

It is noted that in 2014 there is a decrease in the primary incidence of insulin-dependent and insulin-dependent diabetes mellitus in the adult population compared to the previous year. Areas of "risk" in terms of primary incidence of insulin-dependent and insulin-dependent diabetes mellitus are shown in Figure 8.14.

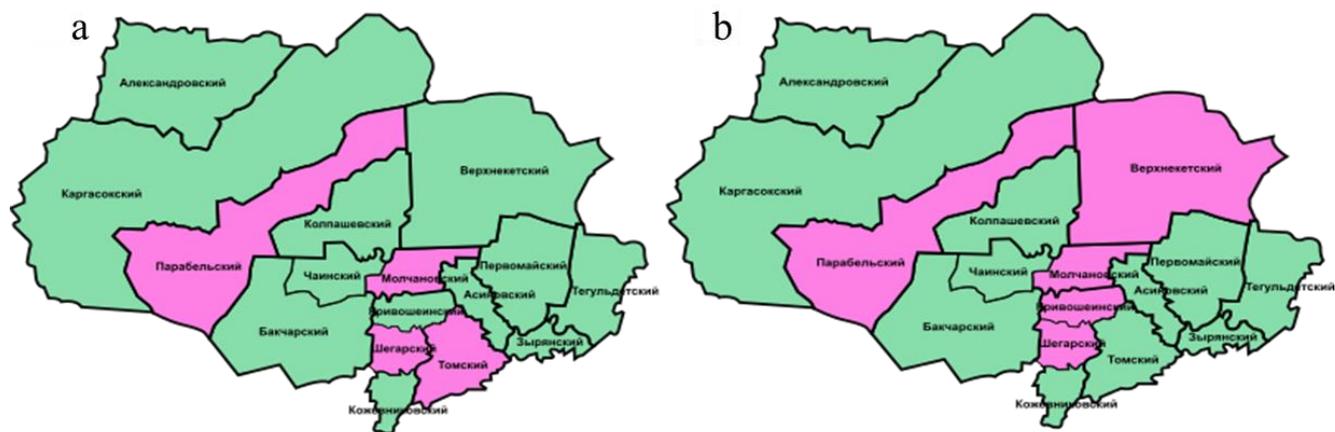


Figure 8.14 - Territory at the "risk" of the level of primary incidence of insulin-dependent (a) and insulin-dependent (b) diabetes mellitus (the figure done by the author on the basis of the data " State report..., 2016").

Note: green - does not exceed the Tomsk region levels; pink - exceeds the Tomsk region levels by 1,5 times or more

In the structure of primary morbidity of the population of the Tomsk region associated with micronutrient deficiencies, a significant proportion were endemic goiter and other forms of nontoxic goiter (53%), thyroiditis accounted for 23%, subclinical hypothyroidism (19%), and thyrotoxicosis (3%). At the same time, the Tomsk region is included in the groups of "risk" territories for the following nosological forms of morbidity: children - endemic goiter associated with iodine deficiency (1.1-1.4 times the average Russian level), congenital iodine deficiency syndrome (exceeding the average Russian level by 1.5 times); adolescents - the same forms of morbidity as children plus other forms of nontoxic goiter, subclinical hypothyroidism, adults - endemic goiter associated with iodine deficiency, as well as subclinical hypothyroidism, thyroiditis (State report..., 2016"). Groups at "risk" of the incidence of the population associated with micronutrient deficiency are shown in Figure 8.15.



Figure 8.15 - Territory at the "risk" of the incidence of the population associated with micronutrient deficiency, with the diagnosis established for the first time. Ranking of the territory according to the average annual indicator (2012-2014) (State report ..., 2016). Note: green – does not exceed the Tomsk region levels; yellow - exceeds the Tomsk region levels by 1,1-1,4 times

Analysis of data on the incidence of the population of the Tomsk region by urolithiasis shows a significant number of districts of the region belonging to the "risk" groups (Figure 8.16).



Figure 8.16 - Territory at the "risk" of the incidence of the urolithiasis disease with a diagnosis established for the first time (State report..., 2016).

Note: green – does not exceed the Tomsk region levels; yellow – exceeds the Tomsk region levels by 1,1-1,4 times; pink - exceeds the Tomsk region levels by 1,5 times or more

The ranking of the administrative districts of the Tomsk region in terms of the overall index of health is of particular interest. As can be seen from Figure 8.17a, eight districts of the region are marked as increased risk groups for violation in the health of the child population, and there are 4 administrative districts in the high-risk zone of the adult population health (Figure 8.17b).

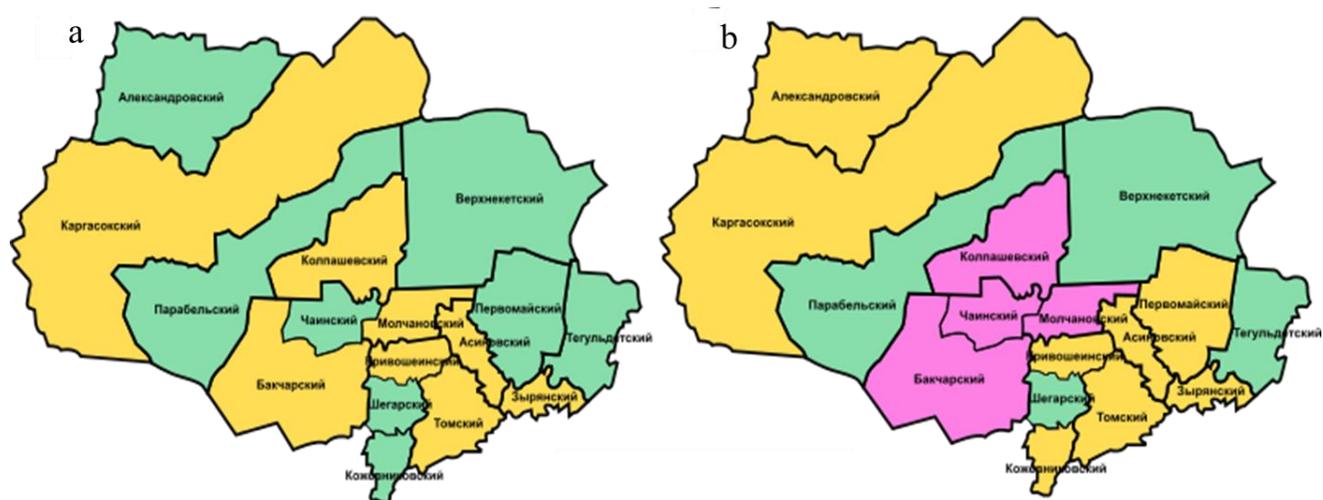


Figure 8.17 - Territory at "risk" on the overall index of health: a - the child population (up to 14 years), b - the adult population (from 18 years and older) (the figure created by the author on the basis of data State report..., 2016).

Note: green – moderate risk; yellow – elevated risk; pink – high risk

Comparison of the "risk" maps of the Tomsk region regarding different types of morbidity data obtained on the toxic effects on human health due to the content of bromine in soils, allows us to draw some conclusions. First of all, it is worth noting that none of the morbidity maps of the Tomsk region is 100% consistent with the results obtained on the total toxicity impact score of bromine on human health (Figure 8.5). The greatest similarity between the maps on morbidity and toxicity of bromine is found in Figure 8.9, reflecting the territory of the "risk" for the overall mortality of the population. Here, maximum mortality rates are recorded in the Bakcharsky and Asinovsky districts

Chapter 8. Estimation of the toxic impact of bromine on ecosystems and human health by ecological modeling of the region, and the lowest in Tomsky district, while the Chainsky, Molchanovsky and Verkhneketsky districts are characterized by average risk levels.

The high level of infant mortality is reflected in the high toxicity of bromine in Kozhevnikovsky and Bakcharsky districts. The latter district also appears at high risk on the integral index of adult health and the high incidence of stomach ulcers, duodenal ulcers, gastritis and duodenitis among children. In addition, in the Tomsky and Zyryansky districts, the low incidence of gastrointestinal and duodenal ulcer, insulin-dependent diabetes mellitus and diseases associated with micronutrient deficiency is reflected in the low total toxicity impact score of bromine on human health in these areas.

Brief conclusion

Thus, the use of the USEtox model allowed us to study the toxic effect of bromine on living organisms both in general, and within different geographic and climatic conditions. The latter is of particular interest in the framework of geoecological research. The model is based on the principles of the methodology of risk assessment, data from laboratory studies, the most important physico-chemical parameters of the elements, features of their bioaccumulation together with many others, are taken into account, which undoubtedly indicates its relevance in assessing the risks to living organisms. The results obtained demonstrate that the toxic effect of bromine on the ecosystem is much higher than on human health. In this case, it differs significantly depending on the component of the environment in which the element is located (soil, air, etc.). The maximum risk for human health is via agricultural soils and air, while for ecosystems it is in fresh water. In addition, the effect of bromine on living organisms in different land-geographical zones varies widely.

The application of the model to assess the toxicity and ecotoxicity of the element in the soils of the Tomsk region allowed us to identify areas of the Tomsk region in terms of risk for ecosystems and human health. One of the drawbacks of the model is the lack of an evaluation scale, indicating the minimum-maximum levels of elements that can be

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dangerous to living organisms. This deficiency was compensated for by comparing the results with other chemical elements, determined by the INAA method and available in the model. As the results show, the risk associated with the presence of bromine in the soils of the Tomsk region is relatively low, both for humans and for ecosystems.

Despite the fact that there are no standards for bromine in soils, and the basic principles of the model are somewhat similar to the principles of sanitary and hygienic standards, the results of the model cannot replace the normative indicators. The results of toxic effects on human health due to bromine content in soils, compared with the maps of the morbidity of the population of the Tomsk region, do not show absolutely identical patterns. However, there is a significant similarity between the toxic effects of bromine on health and the overall mortality of the population. In addition, low/ high levels of bromine toxicity in soils are reflected in the minimum/maximum risk of some types of morbidity in certain districts of the region.

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GENERAL CONCLUSION

A literature review on geoecological aspects of the accumulation and distribution of bromine in natural and technogenic landscapes was performed. It was shown that the distribution of bromine in the components of the biosphere is non-uniform. Maximum element concentrations are observed in the mineral waters and the lowest in river water and atmospheric air.

The quantitative content of the element in various components of the natural environment of the Tomsk region was determined and the results obtained were compared with data on other regions of Russia and abroad, as well as on indicators from literature. Thus, we established that the element's average content in the soils of the Tomsk region exceeds the values observed in the soils of some other regions of Russia and abroad.

An analysis of the spatio - temporal distribution of bromine over the study area, with the designation of local areas characterized by higher contents of the element caused by natural and man - made factors, was carried out. Thus, the territory of the Tomsk oblast was ranked in accordance with the minimum - maximum concentration of the element in environmental compartments. Extremely high levels of bromine accumulation were found in: 1) the sediment of drinking water, children's hair and the blood of residents of Tomsky district; 2) the sediment of drinking water and children's hair of Molchanovsky district; 3) children's hair and altered thyroid glands of the residents of Shegarsky district.

Indicators of the relations of bromine with other chemical elements in the vicinity of industrial enterprises were established. It was found that the levels of accumulation of bromine in environmental compartments tend to decrease with distance from the industrial complexes.

For the first time human toxicity and freshwater ecotoxicity characterization factors for bromine were developed, according to the USEtox model. Results obtained allowed the characterization of human and ecotoxicological impacts of bromine on the samples of soils taken from the Tomsk region, taking into account its landscape-geographical

characteristics, and to analyse these results in conjunction with data and the diseases of the local population. In addition, the ranking of the region's territory according to the degree of risk to ecosystems and human health was performed. Thus, it was found that the highest risk for the health of the inhabitants due to the content of bromine in soils is observed for the Bakcharsky district, whereas the greatest risk for ecosystems was in the Tomsky district.

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7) etc.

RESUME EN FRANÇAIS

Caractéristiques générales de la thèse

Intérêt du sujet

Le brome, contrairement à d'autres éléments chimiques, reste l'un des éléments les moins étudiés à ce jour, bien que des travaux sur les problèmes de son accumulation et de sa migration dans l'environnement aient déjà été réalisés par des chercheurs de différentes disciplines. La plupart des publications disponibles sont spécifiquement consacrées à la prise en compte des caractéristiques naturelles du comportement du brome dans l'environnement. Cependant, une attention accrue devrait être accordée à l'étude de sa techno-géochimie, en raison de la large utilisation de cet halogène dans de nombreuses sphères de l'activité humaine : l'agriculture, la médecine, l'industrie chimique, l'industrie pharmaceutique, l'agroalimentaire, etc.

Le brome est l'un des plus importants éléments participant à la formation de la chaîne trophique : atmosphère - sol - eau naturelle - plantes - animaux - homme. Une «symbiose» de sources naturelles et anthropiques de l'élément détermine la nature complexe et multifactorielle de son entrée dans l'environnement. Cela a, sans aucun doute, une influence sur les caractéristiques d'accumulation et de distribution de l'halogène, à tous les niveaux de la chaîne trophique décrite ci-dessus.

La région de Tomsk (Russie) est particulièrement intéressante du point de vue de l'étude du brome en raison de la présence d'un grand nombre de sources naturelles potentielles (pétrole, gaz, tourbe, charbon, eaux souterraines, y compris les sources d'iode et de brome, etc.) et anthropiques. Ces dernières sont concentrées, principalement, dans le district Tomsky de la région, à savoir dans la zone industrielle du Nord. L'entrée de l'élément dans l'environnement de la région peut également être liée aux émissions des véhicules et au transport aérien dû à la présence de l'aéroport "Bogashevo" qui est l'aéroport international opérationnel d'importance fédérale de la région.

De plus, il est à noter l'importance de choisir le meilleur moyen d'évaluer l'état de l'environnement, ce qui permet de caractériser les effets toxiques des produits chimiques

pour les écosystèmes et la santé humaine. En effet, le brome, du fait de sa toxicité, engendre des impacts négatifs sur les fonctions physiologiques importantes des organismes vivants et participe au développement et à la formation de certains types de maladies. Le brome est l'un des éléments qui conduit le plus souvent à un risque accru pour la santé humaine, au moins 11 pathologies différentes sont associées à l'élément.

La disponibilité d'un nombre important de moyens modernes d'évaluation des impacts environnementaux permet d'effectuer une analyse complète en utilisant diverses méthodes, approches, concepts et modèles qui permettent de prédire les effets néfastes sur les organismes vivants, y compris sur la santé humaine. Du point de vue de l'étude de la toxicité des éléments chimiques, les méthodes de modélisation écologique sont de plus en plus répandues et offrent un certain nombre d'avantages. Par conséquent, ces méthodes présentent un intérêt particulier pour l'étude géoécologique d'un territoire.

Parmi les modèles écologiques existants et permettant d'évaluer les effets toxiques sur les écosystèmes et la santé humaine, le modèle USEtox mérite une attention particulière. Il a été développé par Society of Environmental Toxicology and Chemistry (SETAC) en 2010 et est recommandé par la communauté scientifique mondiale: le PNUE, l'EPA, la Commission européenne et d'autres. L'un des avantages du modèle est la prise en compte de l'effet multifactoriel des éléments chimiques : leur pénétration par inhalation et par voie orale est prise en compte. Un autre avantage important, montrant l'unicité du modèle et sa pertinence dans le contexte des études environnementales, est la prise en compte des caractéristiques géographiques et climatiques spécifiques d'un territoire.

Pour calculer les effets toxiques des éléments chimiques sur les écosystèmes et la santé humaine, il faut connaître leurs facteurs de caractérisation (CF) et leurs masses dans les milieux environnementaux. Les données sur le contenu quantitatif de l'élément sont issues des résultats analytiques et les calculs des CFs s'effectuent selon la méthodologie proposée dans le modèle. De nos jours, la base de données du modèle USEtox comprend des informations sur les CFs pour plus de 3000 composés organiques et 25 éléments inorganiques (As, Cr, Co, etc.). Cependant, il n'y a pas de CF pour le brome, ce qui renforce également la pertinence de cette étude.

L'objectif de l'étude est d'établir les caractéristiques d'accumulation et de distribution du brome dans les composants de l'environnement naturel de la région de Tomsk et de caractériser ses impacts toxicologiques sur la santé humaine et les écosystèmes selon le modèle USEtox.

Tâches principales :

- Faire une revue de la littérature sur les aspects géoécologiques de l'accumulation et de la distribution du brome dans les milieux naturels et anthropisés;
- Déterminer le contenu quantitatif de l'élément dans les différentes composantes de l'environnement naturel sur le territoire de la région de Tomsk et comparer ces données avec l'information sur d'autres régions de la Russie et à l'étranger, ainsi que des sources de littérature.
- Analyser la distribution spatiale du brome sur la zone d'étude et identifier les zones caractérisées par des teneurs élevées en brome, causées par des facteurs naturels et anthropiques;
- Classer les districts de la région de Tomsk conformément en fonction de leur concentration d'élément dans les différentes composantes de l'environnement;
- Analyser les relations entre le brome et les éléments chimiques à proximité des entreprises industrielles;
- Développer les facteurs de caractérisation du brome pour la toxicité humaine et l'écotoxicité en utilisant le modèle USEtox ;
- Caractériser les impacts du brome sur la santé humaine et les écosystèmes sur l'exemple des sols de la région de Tomsk, en tenant compte de ses caractéristiques géographiques et analyser les résultats obtenus avec les données sur les maladies de la population de la région de Tomsk;
- Classer les districts de la région en fonction du degré de risque pour les écosystèmes et la santé humaine.

Assertions

1. Dans le cadre de la circulation du brome dans les systèmes naturels et anthropiques, il est établi que la spécificité de la région de Tomsk est l'accumulation substantielle et la répartition extrêmement hétérogène de l'élément dans les plantes terrestres, les animaux et le corps humain. En ce qui concerne les composants abiotiques, les concentrations du brome les plus élevées significativement sont observées dans les sols des districts de Bakcharsky et Kozhevnikovsky par rapport à la moyenne dans la région, bien que d'autres milieux environnementaux dans ces territoires ne présentent pas de tels niveaux d'anomalie.

2. La spécificité de l'accumulation du brome dans les milieux environnementaux dépend de la nature et de la complexité des impacts naturels et anthropogènes et se manifeste dans les relations associatives de l'élément, l'inégalité de sa concentration au fil du temps et la diminution de son contenu avec la distance de la zone anthropisée.

3. Sur la base des résultats obtenus sur les facteurs de caractérisation du brome, il est établi que la contribution de l'élément à l'indicateur de toxicité est plus élevée pour les écosystèmes que pour la santé humaine. Le classement des districts administratifs de la région de Tomsk en termes d'effet toxique du brome, en tenant compte de ses caractéristiques géographiques, montre que le risque le plus élevé pour la santé des habitants en raison de la teneur en brome dans les sols est observé pour le district Bakcharsky, alors que pour les écosystèmes dans le district Tomsky. Cependant, le brome apporte une contribution minimale au score de toxicité générale.

Collecte et méthodes d'analyses

La dissertation est basée sur les résultats des études, menées personnellement par l'auteur, ainsi que conjointement avec le personnel du Département de géoécologie et de géochimie de l'Institut des ressources naturelles de l'Université polytechnique de Tomsk. Le travail comprend également du matériel fourni par des collègues des universités et instituts de Tomsk (Université d'Etat de Tomsk, Université médicale d'état de Sibérie,

Institut de recherche scientifique en pharmacologie); Pavlodar (Institut pédagogique de Pavlodar); Novorossiysk (Institut de géochimie biochimique, Université fédérale du Sud); Ulan-Ude (Université d'Etat de Buryat) et d'autres.

Dans le cadre de la thèse, la teneur en brome dans 2709 échantillons est considérée. Parmi eux, 408 échantillons de sols, 19 échantillons de charbons, 36 échantillons de sédiments du fond, 8 échantillons d'eau potable, 317 échantillons de dépôts de sel (d'eau potable), 34 échantillons alimentaires ainsi que 1887 échantillons de matières vivantes, y compris des organes, des tissus humains, des espèces de végétation et de mammifères. La principale zone d'échantillonnage est la région de Tomsk, les données d'autres régions de la Russie et de l'étranger ont été considérées pour l'analyse comparative.

Pour la détermination quantitative du brome dans les milieux environnementaux, les méthodes suivantes ont été utilisées : l'analyse instrumentale d'activation neutronique (INAA), la spectrométrie de masse plasmatique à couplage inductif (ICP-MS) et l'analyse par fluorescence X (XRF). Plusieurs échantillons de biomatériaux ont été étudiés à l'aide d'une microscopie électronique à balayage. Tous les matériaux sélectionnés ont été analysés dans des laboratoires accrédités selon des méthodologies certifiées, en utilisant des échantillons de référence standard. La fiabilité des analyses a été confirmée par des déterminations de contrôle sur différents médias, un contrôle interne a été effectué.

Fiabilité des résultats

La fiabilité des résultats est garantie par un nombre statistiquement significatif d'échantillons, analysés par des méthodes analytiques modernes et hautement sensibles dans des laboratoires accrédités.

Contribution scientifique

Pour la première fois, une analyse complète des particularités de l'accumulation du brome dans un nombre significatif de composants environnementaux a été réalisée. Les caractéristiques de la distribution spatiale de l'élément sur le territoire de la région de

Tomsk dans ses différentes conditions naturelles anthropiques sont considérées. En outre, pour la première fois, les facteurs de caractérisation du brome ont été calculés dans le modèle USEtox. Les impacts toxicologiques du brome pour la santé humaine et les écosystèmes ont été établis sur la base des CFs calculées et des résultats des concentrations du Br dans les sols, compte tenu des caractéristiques géographiques de la région de Tomsk. Enfin, un classement du territoire de la région de Tomsk selon le risque pour les écosystèmes et la santé humaine a été réalisé.

Exploitation des résultats

Sur la base des résultats de l'étude, des cartes géochimiques de la distribution du brome dans divers milieux environnementaux ont été créées. La différenciation des districts de la région de Tomsk a été effectuée selon les niveaux de concentration du brome dans l'environnement, ce qui peut être utile pour le suivi géoécologique du territoire.

Les données sur les CFs pour le brome, précédemment non accessibles dans le modèle USEtox, ont été obtenues. À l'avenir, les résultats pour la région de Tomsk en tant que zone géographique distincte, obtenus dans le modèle, peuvent être utilisés pour effectuer des études géoécologiques afin d'étudier la toxicité des éléments chimiques et les risques associés aux écosystèmes et à la santé humaine.

Les résultats du travail ont été utilisés pour mener le cours «Introduction à la science et à l'ingénierie de l'environnement» à l'UTT (France) pour la formation des ingénieurs. Ils pourraient également être utilisés dans les cours «Écologie», «Géochimie de la matière vivante» et «Géologie médicale» pour la préparation des bachelors et des masters dans les spécialités «Écologie et gestion de l'environnement» au Département de géoécologie et de géochimie de l'Institut de Ressources naturelles de l'Université polytechnique de Tomsk.

Approbation des réalisations

Les résultats principaux de la thèse ont été discutés lors des colloques et conférences russes et internationaux:

- Colloque scientifique international des étudiants et jeunes scientifiques de l'académicien M.A. Usov «Problèmes de développement de la géologie et des ressources minérales» (Tomsk, 2011-2013, 2015-2017);
- «Ecologie de la Sibérie méridionale et des territoires adjacents» (Abakan, 2012);
- Conférence internationale scientifique-pratique "Problèmes théoriques et appliqués de la science et de l'éducation (Tambov, 2015);
- II Conférence scientifique russe "Malyshev Readings" (Stary Oskol, 2015);
- IX École internationale de biogéochimie «Biogéochimie de la technogénèse et problèmes contemporains de l'écologie géochimique» (Barnaul, 2015);
- Conférence internationale "Ecodesign" (Tokyo, Japon, 2015);
- Conférence internationale "Radioactivité et éléments radioactifs dans l'environnement" (Tomsk, 2016);
- Conférence internationale "The International Society for Ecological Modeling Global Conference 2016" (Towson, USA, 2016).

En outre, les résultats de la thèse ont été rapportés lors de séminaires scientifiques au département GEGH de TPU (Tomsk, Russie), au CREIDD à l'UTT (Troyes, France), ainsi qu'au Département d'hydrologie et de géochimie de l'Université de Strasbourg (Strasbourg, France).

Au cours de la thèse, l'auteur a également participé à l'école scientifique "Toxicology and Environmental Health" (Utrecht, the Netherlands, 2015) et "USEtox summer school" (Copenhagen, Denmark, 2016).

Publications

Le contenu principal et les résultats scientifiques de la thèse sont publiés dans 20 articles et résumés, dont 2 articles dans les journaux de la liste recommandée par la

Commission d'attestation supérieure de la Fédération de Russie et 1 article en anglais dans un journal avec Facteur d'Impact 2.9, indexé dans la base de données Scopus.

Structure de la thèse et volume

La thèse consiste en une introduction, 8 chapitres, une conclusion et une bibliographie, exposés sur 263 pages de texte dactylographié. Il comprend 78 figures et 33 tableaux. La bibliographie contient 354 sources.

Dans l'introduction, l'intérêt du sujet, l'objectif et les tâches principales, les principaux résultats, la contribution scientifique et l'exploitation des résultats, ainsi que la contribution personnelle de l'auteur et l'approbation des réalisations sont présentés.

Dans le premier chapitre, les caractéristiques écologiques et géochimiques du brome, ses propriétés physico-chimiques, ses effets sur les organismes vivants, ainsi que les normes d'hygiène sont considérés.

Le deuxième chapitre présente une revue approfondie de la littérature sur le brome, les niveaux de son accumulation dans les milieux environnementaux et les principaux domaines d'application de l'élément et de ses composés.

Le troisième chapitre est consacré à l'analyse des méthodes existantes d'évaluation environnementale.

Le quatrième chapitre contient des informations sur les méthodes de recherche, l'échantillonnage et leur préparation, le traitement des données mathématiques et la méthodologie du modèle USEtox.

Le cinquième chapitre considère une brève caractéristique climatique et géoécologique du territoire de la région de Tomsk.

Le sixième chapitre est consacré aux particularités de l'accumulation et de la distribution du brome dans les composants biotiques et abiotiques des milieux environnementaux de la région de Tomsk. L'analyse des niveaux d'accumulation du brome dans les composantes de l'environnement de la région de Tomsk par rapport à d'autres territoires de la Fédération de Russie et à l'étranger est effectuée.

Le septième chapitre présente les caractéristiques de la distribution du brome dans les conditions d'anthropisation du district de Tomsky dans la région. Une analyse de la modification du contenu de l'élément au cours des années a été réalisée. La spécificité géochimique des composants de l'environnement dans les zones près des raffineries de pétrole a été étudiée, ainsi que les relations entre le brome et les autres éléments chimiques.

Le huitième chapitre apporte une analyse des effets toxiques du brome sur les écosystèmes et la santé humaine, en utilisant le modèle d'évaluation environnemental USEtox. L'analyse des interrelations entre la toxicité du brome dans les sols et le niveau de morbidité de la population de la région de Tomsk a été réalisée.

En conclusion, les principaux résultats et conclusions du travail de thèse sont discutés.

Contribution personnelle de l'auteur

La contribution personnelle de l'auteur consiste en la sélection et la préparation de 266 échantillons. L'échantillonnage a été effectué sur le territoire de la région de Tomsk (sols, eau potable, calcaire d'eau potable, cheveux d'enfants, sang humain, microorganismes de sources minérales, végétation, nourriture), dans la région Grand Est en France (sol, eau potable, feuilles de peuplier), et dans la région du Baïkal (microorganismes des sources minérales). En outre, l'auteur a également synthétisé une base de 2433 échantillons.

L'auteur a personnellement procédé au traitement statistique de toutes les données, a donné l'interprétation des résultats obtenus et formulé les assertions proposées. L'auteur a calculé les CFs pour le brome et également introduit la région de Tomsk dans le modèle USEtox en tant que zone géographique distincte, au cours du travail en commun avec P. Fantke et O. Jolliet.

Assertions

Assertion 1. Dans le cadre de la circulation du brome dans les systèmes naturels et anthropiques, il est établi que la spécificité de la région de Tomsk est l'accumulation substantielle et la répartition extrêmement hétérogène de l'élément dans les plantes terrestres, les animaux et le corps humain. En ce qui concerne les composants abiotiques, les concentrations du brome les plus élevées significativement sont observées dans les sols des districts de Bakcharsky et Kozhevnikovsky par rapport à la moyenne dans la région, bien que d'autres milieux environnementaux dans ces territoires ne présentent pas de tels niveaux d'anomalie.

Les caractéristiques naturelles spécifiques de la région de Tomsk (dépôts de sel anciens, ressources d'eau uniques, préservation des conditions de sédimentation continentale tout au long de Mésozoïque et Cénozoïque) ainsi qu'un large nombre de ressources minérales (gisements de lignite, tourbe, hydrocarbures et autres) prédéterminent une accumulation importante du brome dans les composants de l'environnement naturel. De plus, les sources anthropiques jouent aussi un rôle important, notamment par la présence de la plus grande entreprise du cycle du combustible nucléaire du monde, ainsi que la présence de l'une de plus grandes usines de traitement du pétrole du pays. Les deux ont contribué à la formation de sous-provinces biochimiques du brome à caractère technogénique sur le territoire d'étude (Baranovskaya, 2003).

En général, en comparaison avec les données de la littérature, pour l'oblast de Tomsk les niveaux d'accumulation du brome significativement les plus élevés sont observés dans les eaux douces (plus de 40 mg/kg), les plantes terrestres (plus de 60 mg/kg) et dans les organismes animaux (environ 300 mg/kg). Une teneur élevée de l'élément est également observée dans le corps humain, mais sa concentration est observée non dans les cheveux et les poumons (ce qui est noté dans la littérature), mais plus dans le sang, les reins, l'aorte, la thyroïde, etc. (Figure 1).

Par ailleurs, les produits d'alimentation (18 types) utilisés par les habitants de la région de Tomsk ne dépassent pas les concentrations en brome observées dans la

littérature et, par conséquent, ne représentent pas un facteur prédominant dans l'accumulation de l'élément dans le corps humain.

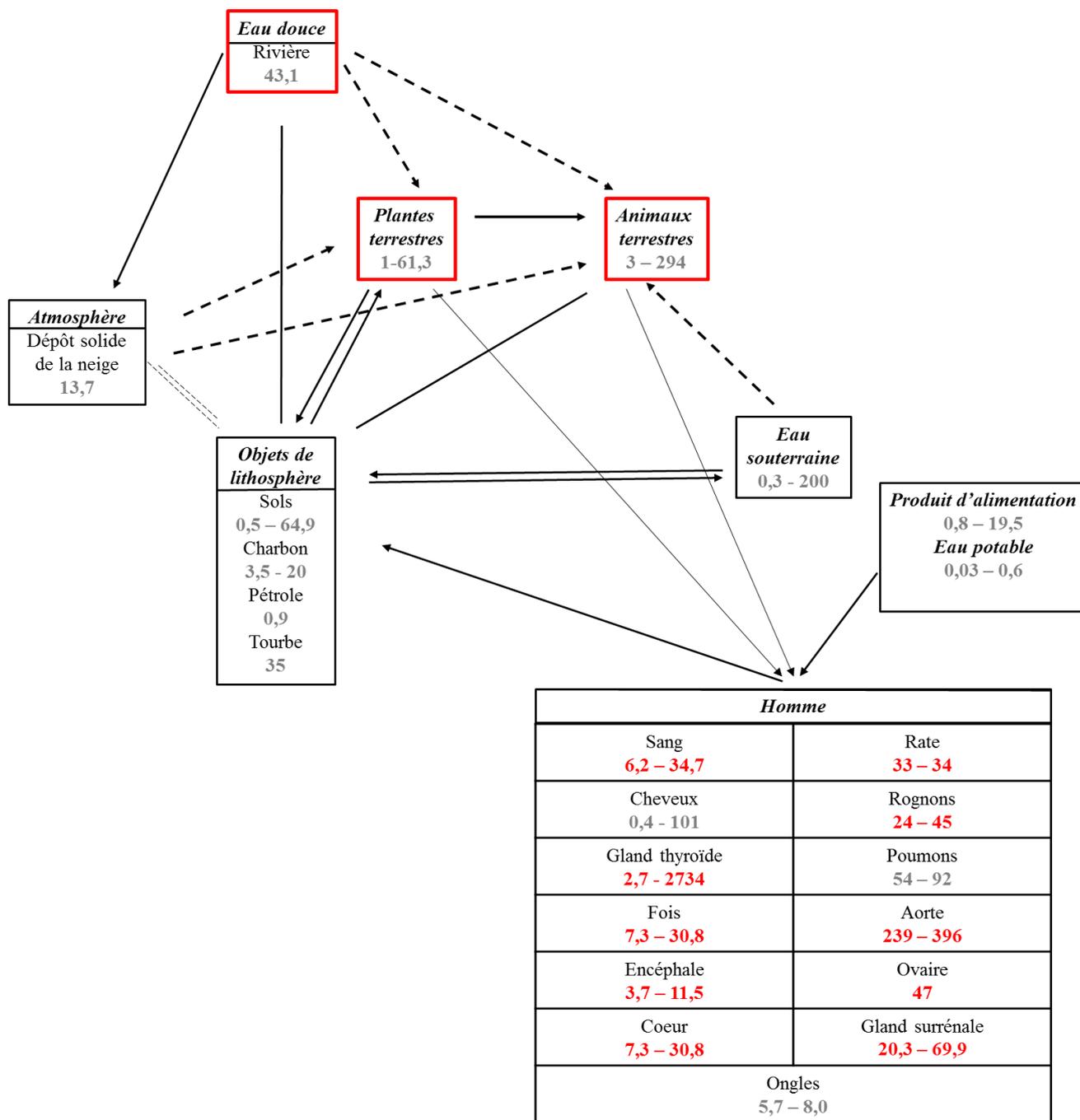


Figure 1 – Schéma simplifié de la distribution du brome dans l'environnement de la région de Tomsk dans le cycle normal de l'élément dans la nature, en mg/kg (pour les objets d'hydrosphère – en mg/l)

Note: les données sur les eaux douces et souterraines sont issues de Kolubaeva, 2015 (selon l'auteur, les données de l'eau correspondent à un niveau d'arrière-plan et sont considérées comme caractéristiques de zones écologiquement propres); sédiments solides de neige (régions d'arrière-plan

de Sibérie occidentale) – selon Shatilov, 2001; tourbe – selon Mezhibor, 2009, pétrole – selon Rikhvanov et al, 2015.

Contrairement aux substances bio-abiotiques et biogènes, sur l'exemple desquelles nous observons l'homogénéité géochimique de l'accumulation du brome, pour les organismes vivants, on observe un certain chaos géochimique (Figure 2). L'accumulation géochimique chaotique de l'halogène se reflète clairement dans les plages de concentration de 18,3 mg/kg chez les microorganismes à 144 mg/kg chez les animaux terrestres, avec une différence du coefficient de variation de 120 à 474% et une variabilité maximale étant dans les cheveux des enfants. Cela indique que les organismes vivants sont capables de concentrer des quantités très élevées de l'élément et peuvent être des indicateurs des changements qui ont lieu dans la nature, sous l'influence des facteurs naturels et anthropiques.

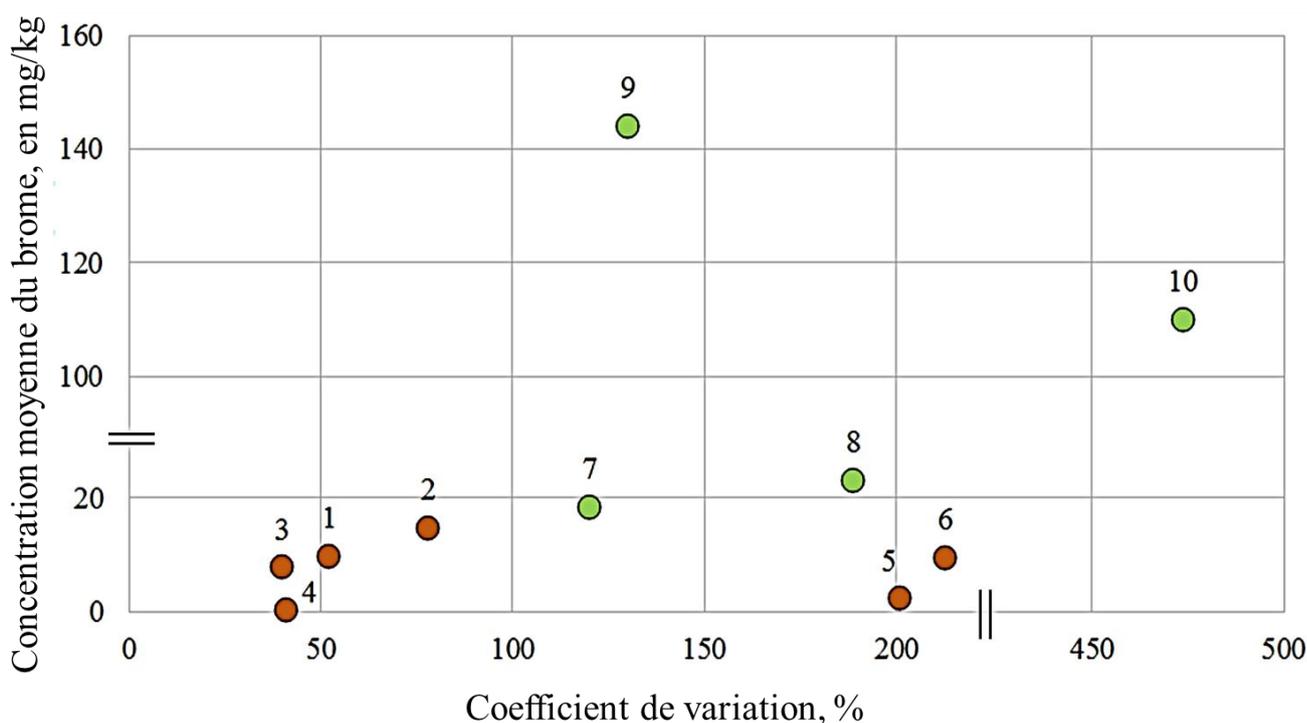


Figure 2 – Niveaux d'accumulation du brome (teneur moyenne) dans les composants abiotiques et biotiques de l'environnement de la région de Tomsk, mg/kg

Note: 1 – charbon, 2 – sols, 3 – sédiments du fond, 4 – eau potable (mg/l), 5 – calcaire d'eau potable, 6 – sédiments solides (données pour la région de Sibérie Ouest, selon Shatilov, 2001), 7 – microorganismes de sources minérales, 8 – organismes végétaux, 9 – organismes animaux, 10 – corps humain; en marron les composants abiotiques, en vert – biotique.

On constate que la teneur en brome dans les charbons, les sols, l'eau potable et les sédiments de la région ne dépasse pas 20 mg/kg (mg/l pour l'eau potable) avec un coefficient de variation relativement faible : pour tous les objets, il n'est jamais au-delà de 50%, hormis pour les sols – 79%. Une attention particulière est à apporter au dernier, puisqu'il constitue l'un des premiers liens dans la migration biogéochimique des éléments chimiques.

Ainsi, l'analyse des paramètres statistiques (Tableau 1) et la répartition spatiale du brome dans les sols de la région de Tomsk (Figure 3) montre que la teneur en halogène minimale est enregistrée dans les sols de Tomsky district, et les maximales – dans les sols des districts Kozhevnikovsky et Bakcharsky. Il faut également noter que dans le dernier, des niveaux élevés d'accumulation de l'élément dans les sols sont observées dans 18 villages étudiées. Cette particularité ne se reflète pas dans l'étude d'autres objets (calcaire d'eau potable, les cheveux des enfants, le sang, les tissus de la thyroïde malade).

Tableau 1 – Paramètres statistiques de la distribution du brome dans les sols de la région de Tomsk, mg/kg

District	N	X	λ	Min	Max	Mo	Me	V,%
Parabelsky	6	14,8	1,7	9,0	22,1	–	14,5	29
Kolpashevsky	6	11,9	2,1	7,5	21,3	–	10,4	43
Chainsky	16	15,3	2,0	5,0	31,8	5,0	13,1	54
Molchanovsky	5	14,5	1,1	11,1	18,0	–	14,4	17
Krivosheinsky	2	16,8	–	13,0	20,1	–	–	–
Shegarsky	2	14,3	–	13,0	15,6	–	–	–
Kozhevnikovsky	33	29,8	1,5	0,5	35,8	–	18,8	47
Tomsky	182	9,1	0,4	0,5	59,5	0,5	8,9	65
Asinovsky	15	19,7	1,8	5,0	31,8	23,4	20,8	35
Pervomaysky	5	15,6	3,2	5,0	23,9	14,4	14,4	46
Verkhneketsky	14	13,6	2,2	4,4	30,1	–	10,7	60
Teguldetsky	20	13,2	1,4	5,0	28,0	5,0	12,4	48
Zyriansky	44	10,8	1,0	3,9	34,4	6,1	8,6	62
Bakcharsky	39	40,3	1,9	15,2	64,9	–	41,3	29
<i>Tomsk region</i>	<i>389</i>	<i>14,5</i>	<i>0,6</i>	<i>0,5</i>	<i>64,9</i>	<i>0,5</i>	<i>11,1</i>	<i>79</i>

Note: il n'y a pas de données sur les district Alexandrovsky et Kargasoksky ; N – nombre d'échantillons; X – valeur moyenne; λ – erreur type; Min et Max – valeurs minimales et maximales, respectivement, Mo – Mode, Me – médian, V – coefficient de variation.

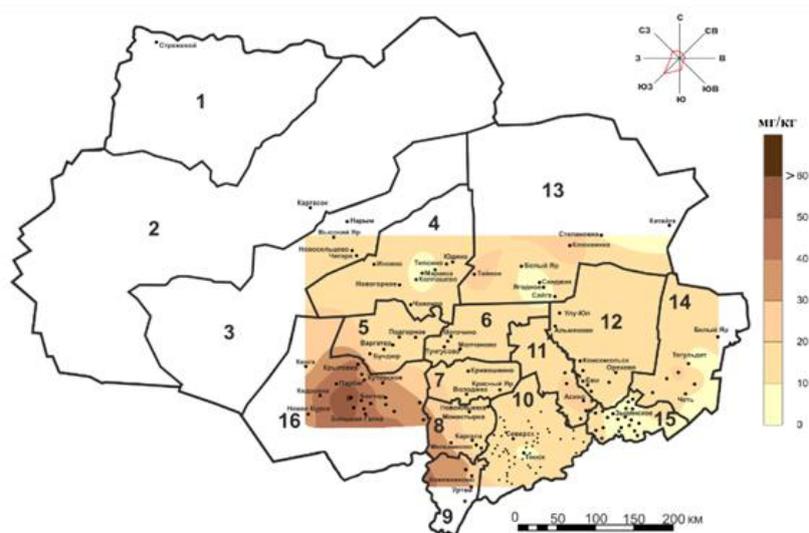


Figure 3 - Carte schématique de la distribution du brome (mg/kg) dans les sols de la région de Tomsk

Note (districts): 1 – Aleksandrovsky, 2 – Kargasovsky, 3 – Parabelsky, 4 – Kolpashevsky, 5 – Chainsky, 6 – Molchanovsky, 7 – Krivosheinsky, 8 – Shegarsky, 9 – Kozhevnikovsky, 10 – Tomsky, 11 – Asinovsky, 12 – Pervomaysky, 13 – Verkhneketsky, 14 – Teguldetsky, 15 – Zyriansky, 16 – Bakcharsky.

L'analyse des données disponibles dans la littérature (Gavshin, 1984, Mironov, Zhmodik 1991, Bakiev, 2006, Belkin, 2017) suggère une possible genèse naturelle du brome dans les sols de Kozhevnikovsky et Bakcharsky districts. Cela peut être liée à l'entrée de l'élément sous forme de fluides/gaz avec des saumures via des structures perméables. Cette question nécessite une étude plus approfondie.

Assertion 2. La spécificité de l'accumulation du brome dans les milieux environnementaux dépend de la nature et de la complexité des impacts naturels et anthropogènes et se manifeste dans les relations associatives de l'élément, l'inégalité de sa concentration au fil du temps et la diminution de son contenu avec la distance de la zone anthropisée.

Compte tenu du fait que le brome est un élément spécifique de l'industrie pétrochimique (Shatilov, 2001; Yazikov, 2006; Baranovskaya, 2011, etc.), afin d'établir la spécificité géochimique des milieux naturels à proximité des installations de la raffinerie, nous avons étudié les milieux naturels et biomatériaux sélectionnés aux alentours de ce type d'entreprise. En 2014, de l'eau potable, du sol et des feuilles de

peupliers ont été sélectionnées dans la région Grand Est de la France, où une grande raffinerie de pétrole se situe. Les mêmes objets de recherche, ainsi que le calcaire de l'eau potable et les cheveux des enfants ont également été sélectionnés, à la même année, dans plusieurs villages de la zone industrielle de Tomsk-Seversk, où se situe la plus grande usine pétrochimique en Russie, ainsi qu'un certain nombre d'autres entreprises industrielles.

L'analyse de l'information obtenue montre que le brome est concentré spécifiquement et localement dans des milieux naturels du territoire étudié (Tableaux 2-4).

Tableau 2 - Série géochimique d'éléments chimiques dans l'eau potable dans les zones de localisation des raffineries de pétrole

Territoire		Série géochimique d'éléments chimiques
Communes du district Tomsky	Samus	(Rb,In) _{1,8} Ba _{1,6} Sc _{1,4} (Na Cu) _{1,3} (Si,K,Sr) _{1,1}
	Naumovka	Mn _{3,7} B ₃ Pb _{2,6} Co _{2,4} Fe _{2,1} (Cu Zn) _{1,8} Cr _{1,2} (Ca Sc Rb,Sb) _{1,1}
	Kuzovlevo	Sb _{1,5} Br_{1,4} Cu _{1,3} (Ca Zn) _{1,2} (Mg I) _{1,1}
	Zonal'naya stantsiya	Sb _{1,5} Co _{1,4} (Ca,Li,Ba) _{1,3} (Si,Sr) _{1,2} (B,Na,Mg,Cr) _{1,1}
	Kopylovo	U _{4,8} Mo _{3,7} Li _{2,3} K _{1,8} (Ti,Cs) _{1,7} Br_{1,4}
France	Région Grand-Est	Al _{3,2} I _{2,6} Br_{2,3} B _{1,7} V _{1,5} (Be,U) _{1,4} (Na,Ti) _{1,3} Ce _{1,2} Fe _{1,1}

Note: Ici et dans les tableaux ci-dessous les coefficients de concentration ont été calculés par rapport à la moyenne de l'échantillon

Sur le territoire du district Tomsky dans la zone d'influence de la raffinerie de pétrole, le brome se trouve dans les eaux potables des communes de Kuzovlevo et Kopylovo. La première d'entre elles est à proximité des principales installations de production, et la seconde est un point de jonction pour le transport des produits pétroliers. Nous ne prétendons pas juger les moyens de pénétration du brome dans l'eau potable et les spectres des éléments obtenus, qui sont concentrés dans l'eau. Mais ces résultats préliminaires nécessitent une étude approfondie à l'avenir, tant du point de vue du facteur naturel de formation de ses eaux que du facteur d'anthropisation du territoire étudié.

La nature complexe du territoire, affectée par les activités de l'agglomération industrielle Tomsk-Seversk, se traduit par une très large gamme d'éléments qui sont concentrés dans des feuilles de peuplier (Tableau 3).

Tableau 3 - Série géochimique d'éléments chimiques dans les feuilles de peuplier dans les zones de localisation des raffineries de pétrole

Territoire		Série géochimique d'éléments chimiques
Communes du district Tomsky	Samus	$\text{Sn}_5\text{Hg}_{1,8}(\text{B},\text{Na},\text{K})_{1,5}(\text{Ge},\text{Sr},\text{Au},\text{Pb})_{1,4}(\text{Ba},\text{W})_{1,3}(\text{Mg},\text{Co},\text{Si},\text{Sb})_{1,2}$
	Naumovka	$\text{Be}_3(\text{Ni},\text{Rb},\text{Cd})_2\text{Zn}_{1,7}\text{Ag}_{1,6}(\text{Sm},\text{Eu})_{1,5}(\text{Dy},\text{Pr},\text{Gd},\text{Tb},\text{Br})_{1,4}(\text{Cu},\text{As},\text{Y})_{1,3}(\text{Mn},\text{Er},\text{La},\text{Ho},\text{Nd},\text{Yb})_{1,2}(\text{Ca},\text{Cr},\text{Co},\text{Se},\text{Cs},\text{Ba},\text{Lu},\text{Hg})_{1,1}$
	Kuzovlevo	$(\text{Ce},\text{Tl})_{1,7}\text{Be}_{1,6}(\text{Cd},\text{Ge})_{1,5}\text{Tm}_{1,4}(\text{Eu},\text{Gd},\text{Y},\text{La},\text{Pr},\text{Nd},\text{Tb},\text{Ho},\text{Er})_{1,3}(\text{Mg},\text{Sc},\text{Ni},\text{Co},\text{Ba},\text{Dy})_{1,2}(\text{P},\text{Ca},\text{Mn},\text{Sr},\text{Sm},\text{Yb})_{1,2}$
	Zonal'naya stantsiya	$\text{Se}_{2,2}\text{Br}_{1,9}\text{V}_{1,6}(\text{Ti},\text{Sb},\text{Bi})_{1,5}\text{W}_{1,4}(\text{Li},\text{Zr},\text{Pt},\text{Th})_{1,3}(\text{Cr},\text{Nb},\text{U})_{1,2}(\text{Mg},\text{Fe},\text{Ga},\text{As},\text{Pb})_{1,1}$
	Kopylovo	$\text{I}_4\text{Ta}_{3,2}\text{Mo}_{2,9}\text{Au}_{2,6}(\text{Al},\text{Th})_{2,2}(\text{Li},\text{Hf})_{2,1}(\text{Nb},\text{V},\text{Li},\text{U})_{1,9}(\text{Cs},\text{Ti})_{1,8}(\text{Ga},\text{Zr})_{1,7}(\text{Sc},\text{Lu})_{1,5}\text{Na}_{1,4}(\text{P},\text{Fe},\text{Ce},\text{Tb},\text{Dy},\text{Yb},\text{Er},\text{Hg},\text{Pt},\text{Pb})_{1,2}(\text{Cr},\text{Nd},\text{Ho},\text{Tm},\text{Gd},\text{As})_{1,1}$
France	Grand-Est region	$\text{Br}_{22}\text{Na}_{19,7}\text{Zr}_{14,8}\text{Au}_6\text{Se}_5\text{Sb}_4\text{I}_{3,5}\text{Ta}_{3,2}\text{V}_{2,4}\text{U}_{2,3}(\text{Nb},\text{Hf})_2(\text{Si},\text{Ca})_{1,9}(\text{Ti},\text{P})_{1,6}\text{Fe}_{1,4}(\text{As},\text{Ag},\text{Tl})_{1,3}(\text{K},\text{Zn},\text{Pb})_{1,1}$

Le village Kopylovo est caractérisé par le spectre maximum d'éléments avec des accumulations moyennes supérieures dans les feuilles de peuplier, avec un coefficient de concentration du brome égal à 0,2. En général, le brome ne fait pas partie des éléments typiques des arbres de ce territoire, alors qu'en France, dans la zone de la raffinerie, ses concentrations sont assez grandes et 5 fois plus élevées que la valeur moyenne.

Dans les sols des communes du district de Tomsky, les coefficients de concentration du brome supérieurs à 1 ne sont observés que dans le village Zonal'naya Stantsiya (Tableau 4), où, avec le village Naumovka, la gamme maximale d'éléments chimiques est trouvée. L'accumulation d'un nombre considérable d'éléments chimiques est également caractéristique pour les sols français, dans lesquels le brome s'accumule au-dessus des concentrations moyennes.

Tableau 4 - Série géochimique d'éléments chimiques dans les sols dans les zones de localisation des raffineries de pétrole

Territoire		Série géochimique d'éléments chimiques
Communes du district Tomsky	Samus	$Ru_{1,8}(Ca,Si)_{1,2}(Se,Pb)_{1,1}$
	Naumovka	$(Cs,Li,V)_{1,5}(Cr,Fe,Ni,As)_{1,4} (Mg,I,Y,Ce,Pr,Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, W, Tl, Bi, Th, U)_{1,3} (Al, Co, Cu, Ga, Rb, Zr, Nb, Mo, La, Hf, Ta)_{1,2} (Ti, Sn, Ba)_{1,1}$
	Zonal'naya stantsiya	Br $_{1,9}(Na,I)_{1,4}Se_{1,3} (Mg, Ti, Mn, Co, Nb, La, Ce, Pr, Nd, Sm, Dy, Er, Yb, Ta, Th)_{1,2} (Al, V, Cr, Fe, Ga, Sr, Y, Zr, Sn, Eu, Gd, Tb, Ho, Lu, Hf, W)_{1,1} (B, Na, Mg, Cr)_{1,1}$
	Kopylovo	$(Zn,P)_2Ag_{1,9}(Mn,Sb)_{1,4}(Ca,Cu,Sn)_{1,3}Sr_{1,2} (Ti, Ge, Se, Nb, Mo, Ta)_{1,1}$
France	Grand-Est region	$W_{5,7}I_2Hf_{1,8}(Ni,Zr)_{1,7}(Sn,La,Th)_{1,5}(Ce,Pb,U)_{1,4} (Ca, As, Se, Nb, Ag, Pr, Nd, Sm, Ta, Tl)_{1,3}(Cs, Br)_{1,2} (Li, Si, Ti, Rb, Y, Gd, Ho, Er, Tm, Yb, Lu)_{1,1}$

Par conséquent, nous pouvons conclure qu'il y a une «diversification» des accumulations du brome ainsi qu'un comportement complexe dans les milieux naturels sous différentes conditions naturelles-anthropiques. Dans les zones soumises à une influence complexe naturelle et technogénique, il y a une hétérogénéité d'accumulation d'élément, qui peut être causée par des comportements compensatoires de médias étudiés qui accumulent des quantités importantes de divers éléments chimiques, y compris ceux qui déplacent le brome dans les séries géochimiques.

Le caractère naturel-technogénique complexe de la zone industrielle de Tomsk est fortement reflété dans l'étude de la relation du brome avec d'autres éléments chimiques. Comme l'antimoine, à la manière du brome, est un élément spécifique de l'industrie pétrochimique, nous avons examiné la relation Br/Sb dans des milieux naturels et des biomatériaux dans les zones d'emplacement des complexes pétrochimiques (Figure 4). Les différences dans cette relation sont clairement enregistrées dans l'étude des feuilles de peuplier, où les villages de la région de Tomsk sont séparés en groupes lorsque le ratio est 254-3588, tandis qu'il est de 7000 pour le territoire de la France. En outre, les ratios Na/Br, Br/Pb, Br/U, Br/I dans les milieux naturels présentent une ambiguïté d'indicateurs obtenus pour les différents milieux d'environnement des villages de la zone industrielle, qui est largement différent de ceux de la zone de mono production.

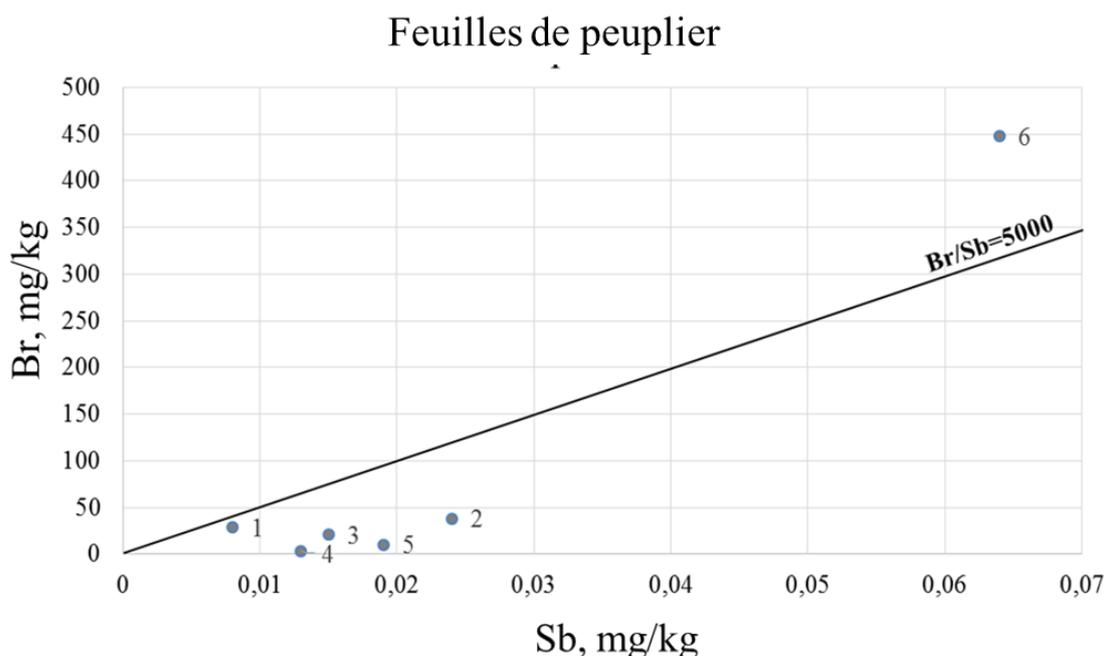


Figure 4 - Ratios Br/Sb dans des feuilles de peuplier à proximité de complexes de raffinage du pétrole

Note: 1 – Naumovka, 2 – Zonal'naya stantsiya, 3 – Kopylovo, 4 – Kuzovlevo, 5 – Samus, 6 – France

Sur les deux territoires, quelle que soit l'étendue de la charge naturelle et anthropique, il y a une tendance à la baisse des concentrations du brome dans les milieux d'environnement à la distance de la zone d'impact anthropique avec des associations géochimiques d'éléments spécifiques pour chaque milieu (Tableau 5).

Tableau 5 - La tendance à l'accumulation du brome en fonction de la distance de la zone industrielle et les associations géochimiques du brome avec des éléments chimiques dans les objets d'étude

Objet d'étude	Tendance à l'accumulation du Br selon la distance de la zone industrielle (< 30 km – > 30 km)	Association géochimique du brome significatives
Calcaire d'eau potable	↘	Eu (0,85), La (0,87) à un niveau de signification 0,21
Cheveux d'enfants		La (0,62), Ag (0,27), Co (0,15) à un niveau de signification 0,13
Sang		Hf (0,74), Th (0,71), Ce (0,88), La (0,74) à un niveau de signification 0,16
Thyroïde		Ce (0,41) à un niveau de signification 0,34

Organes et tissus du porc domestique (<i>Sus scrofa domestica</i> Linnaeus 1758)	U (0,59), Na (0,81) à un niveau de signification 0,32
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Comme le montre la Figure 5, le brome est caractérisé par une accumulation irrégulière qui peut être causée par différentes intensités d'émissions. De plus, on observe une tendance de forte réduction des concentrations d'éléments en 2014. Cela peut être dû à l'arrêt des réacteurs de l'usine chimique, qui est une source potentielle d'émissions du brome dans l'environnement (Baranovska, Rikhvanov 2002, Baranovska, 2003) et un changement dans la nature de la production dans l'entreprise ainsi que d'une intensité de la production de l'usine pétrochimique.

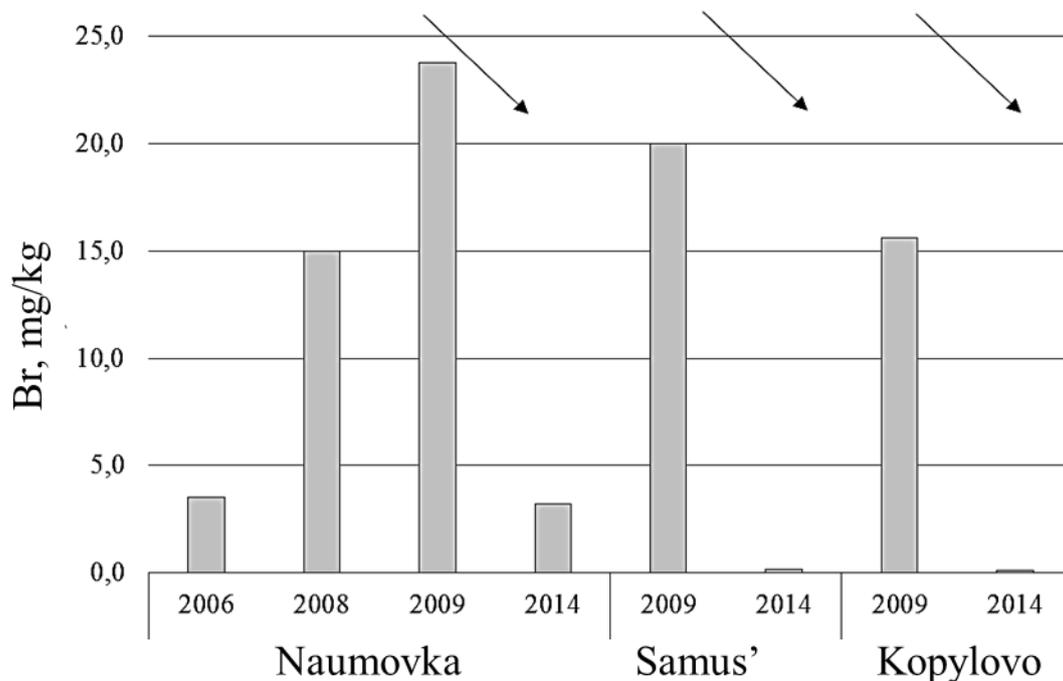


Figure 5 - Variation de la teneur en brome avec les années dans les cheveux des enfants, qui vivent dans les communes situées près de la zone industrielle, mg/kg

Il y a une différence significative dans l'accumulation de l'élément dans la zone industrielle par rapport aux sources de la littérature et aux données générales pour la région de Tomsk. La concentration du brome dans les cheveux des enfants vivant à proximité de la zone industrielle est plus de 9 fois plus élevée que la concentration de l'élément chez les enfants du district Tomsky (hors de cette zone) et 12,5 fois plus élevée dans le sang des résidents. La teneur en brome dans les tissus pathologiquement modifiés de la glande thyroïde du district Tomsky se caractérise par des concentrations d'éléments

beaucoup plus élevés que les données des sources de la littérature : ils sont 62 fois plus élevés. Toutefois, ils sont inférieurs aux niveaux d'accumulation maximale observés dans la glande thyroïde dans la région de Tomsk, en général, en raison de concentrations anormalement élevées de l'élément dans ce substrat biologique des habitants du district Shegarsky. La teneur en brome dans les organes et les tissus des animaux terrestres aux alentours de la zone industrielle est 4 fois plus élevée que les concentrations typiques de la région de Tomsk et 4,5 fois plus élevée pour les plantes terrestres. De plus, les niveaux d'accumulation élevés d'élément sont également observés pour les eaux douces de la région par rapport aux données sur les territoires d'arrière-plan.

Assertion 3. Sur la base des résultats obtenus sur les facteurs de caractérisation du brome, il est établi que la contribution de l'élément à l'indicateur de toxicité est plus élevée pour les écosystèmes que pour la santé humaine. Le classement des districts administratifs de la région de Tomsk en termes d'effet toxique du brome, en tenant compte de ses caractéristiques géographiques, montre que le risque le plus élevé pour la santé des habitants en raison de la teneur en brome dans les sols est observé pour le district Bakcharsky, alors que pour les écosystèmes dans le district Tomsky. Cependant, le brome apporte une contribution minimale au score de toxicité générale.

Les facteurs de caractérisation de la toxicité humaine et de l'écotoxicité, calculés par l'auteur, sont présentés dans les figures 6 et 7, respectivement. Comme on le voit sur ces graphiques, les facteurs de caractérisation de la toxicité varient en fonction des types de milieux impactés. Les résultats obtenus ont permis de conclure que la contribution du brome à l'indicateur de toxicité pour les écosystèmes est plus élevée que pour la santé humaine. Le plus grand risque pour les écosystèmes, dû à la pollution au brome, est observé pour l'eau douce. L'impact pour les sols est le même, quel que soit leur type. Contrairement à la toxicité du brome pour les écosystèmes, au niveau de l'impact sur la santé humaine, l'élément est plus dangereux via la pollution des sols utilisés à des fins agricoles. L'élément peut également avoir un effet toxique sur la santé humaine via l'air. Parmi tous les composants environnementaux étudiés, le brome dans les sols naturels et l'eau de mer a moins d'effet sur les humains.

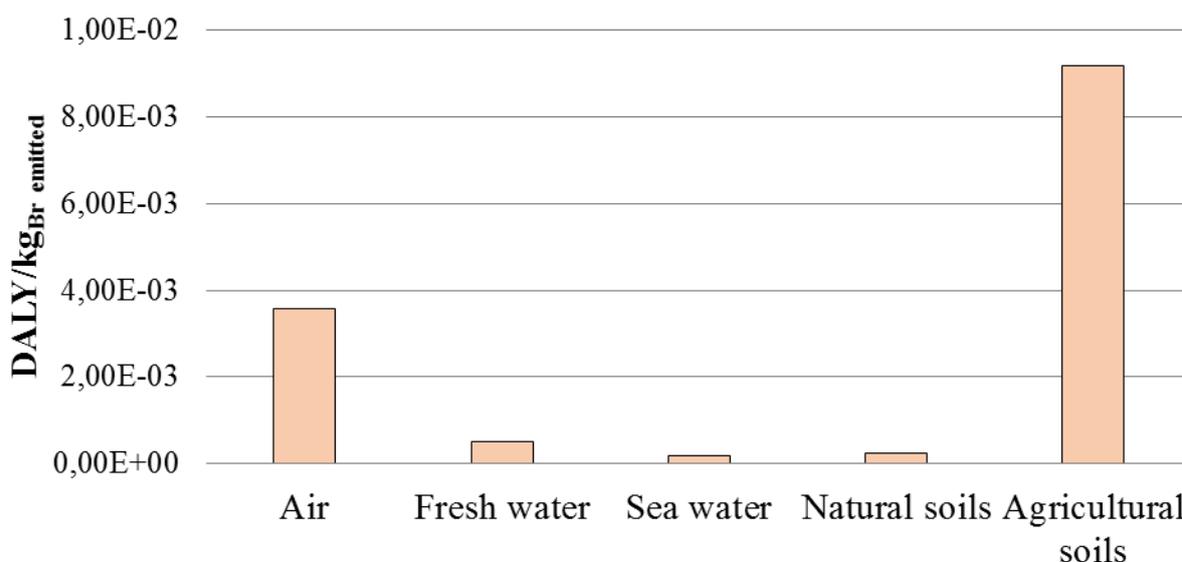


Figure 6 - Facteurs de caractérisation de la toxicité du brome pour la santé humaine, $DALY/kgBr_{emitted}$

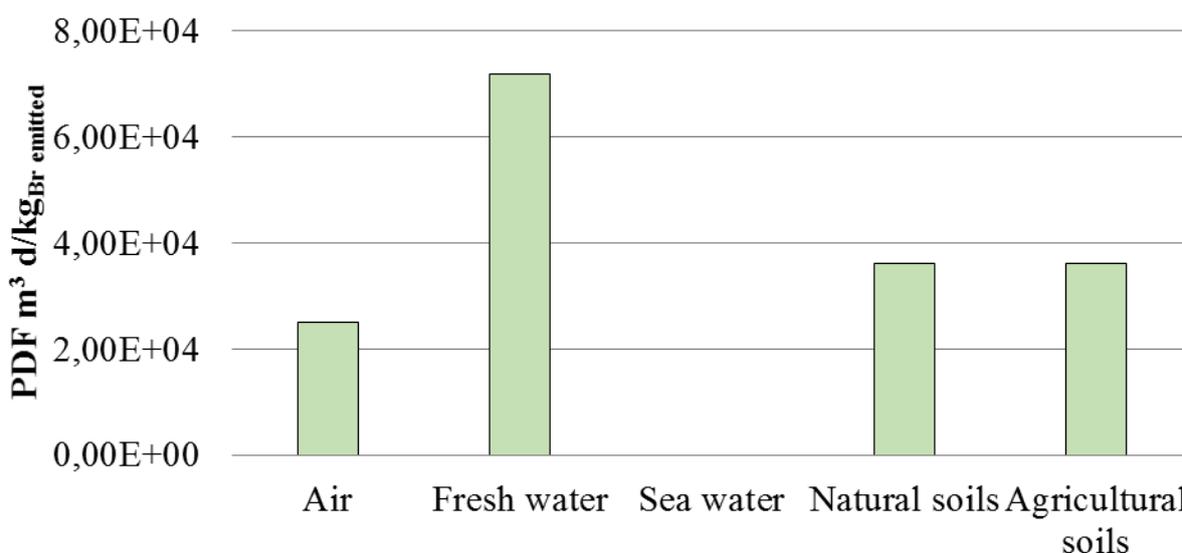


Figure 7 - Facteurs de caractérisation de la toxicité du brome pour les écosystèmes, $PDF m^3d/kgBr_{emitted}$

De manière générale, on peut conclure que les résultats obtenus dans le cadre de la modélisation ne contredisent pas l'information issue de la littérature. Selon la modélisation, dans l'eau de mer l'élément n'est effectivement pas dangereux pour les écosystèmes, ce qui, à notre avis, est logique, étant donné que les organismes marins sont capables d'accumuler des concentrations élevées d'éléments sans aucun effet. Sur la base de ces résultats, la même conclusion peut être formulée sur la toxicité du brome

pour la santé humaine. L'effet toxique élevée, associée à des sols agricoles, peut être connectée à l'utilisation de divers pesticides. L'impact causé par l'inhalation est largement connu et se reflète dans les documents réglementaires.

En utilisant l'exemple des sols dans la région de Tomsk, nous démontrerons clairement l'utilisation possible du modèle USEtox pour déterminer les effets toxiques sur les écosystèmes et la santé humaine. Nous notons également la possibilité de réaliser un classement des zones de la région en termes de degré de risque. Les résultats de la détermination quantitative du brome dans les sols de la région de Tomsk par la méthode INAA, ainsi que les facteurs de caractérisation du brome calculés pour les écosystèmes et les humains dans la région de Tomsk ont servi de base pour le calcul du score d'impact de la toxicité. Les résultats obtenus sont présentés dans le Tableau 6.

Tableau 6 - Scores d'impact de la toxicité pour l'homme et les écosystèmes dans la région de Tomsk

№	District	Concentration du Br dans les sols, mg/kg (selon les résultats de INAA)	Scores d'impact de la toxicité	
			Pour les hommes, <i>CTUhum</i>	Pour les écosystèmes, <i>CTUeco</i>
3	Parabelsky	14.8	74.53	9.3×10^5
4	Kolpashevsky	11.9	59.93	7.5×10^5
5	Chainsky	15.3	77.05	9.6×10^5
6	Molchanovsky	14.5	73.02	9.1×10^5
7	Krivosheinsky	16.8	84.61	1.1×10^6
8	Shegarsky	14.3	72.02	9.0×10^5
9	Kozhevnikovsky	29.8	150.08	1.9×10^6
10	Tomsky	9.3	41.01	1.2×10^7
11	Asinovsky	19.7	99.21	1.2×10^6
12	Pervomaysky	15.6	78.56	9.8×10^5
13	Verkhneketsky	13.6	68.49	8.5×10^5
14	Teguldetsky	13.2	66.48	8.3×10^5
15	Zyriansky	10.8	54.39	6.8×10^5
16	Bakcharsky	39.4	198.42	2.5×10^6
17	<i>Tomsk region (moyenne)</i>	<i>14.6</i>	<i>73.53</i>	<i>9.1×10^5</i>

L'effet toxique minimal du brome sur la santé humaine, en raison de la teneur de l'élément dans les sols, est observé dans les districts Kolpashevsky, Zyriansky et

Tomsky. Cela est dû, principalement, à des concentrations faibles de l'halogène dans les sols. Un risque accru pour la santé humaine est observé dans les districts Kozhevnikovsky et Asinosky, et le plus haut dans Bakcharsky, où il y a des teneurs maximales d'accumulation du brome dans le sol. Lorsque l'on compare les résultats avec 5 autres éléments chimiques (Cr, As, Ag, Sb, Ba), disponibles dans la base de donnée du modèle USEtox, il est évident que le brome n'est pas le plus grand contributeur aux effets toxiques sur la santé humaine (il s'agit notamment du chrome, de l'arsenic, etc.). La contribution du brome à la toxicité totale dans différents districts de la région varie de 0,5% à 21,6%.

Les effets toxiques du brome pour les écosystèmes sont significativement différents de son impact sur la santé humaine. L'impact minimal sur les écosystèmes, en raison de la teneur de l'élément dans le sol, est observé dans un certain nombre de districts de la région : Parabelsky, Kolpashevsky, Molchanovsky, Shegarsky, Verkhneketsky, Teguldetsky et Zyryansky. Dans le district Bakcharsky, où l'impact potentiel sur la santé humaine est le plus élevé, les effets sur les écosystèmes ne sont en revanche pas les plus élevés. Il est à noter une situation particulière pour la district Tomsky dans lequel l'effet toxique sur la santé humaine est minimale alors qu'il est maximal sur les écosystèmes. Lorsque l'on compare les résultats avec 9 autres éléments chimiques (Cr, Co, As, Sr, Ag, Sb, Cs, Ba, Fe), il a été révélé que le brome n'a pas la plus grande contribution aux effets toxiques, la contribution duquel est comprise entre 1,9% et 8,6%.

L'analyse des données de morbidité (mortalité globale et infantile, mortalité par cancer, incidence de l'ulcère gastrique et ulcère duodéal, gastrite et duodénite, non insulino-dépendant, diabète et insulino-dépendant, etc.) de la population de la région de Tomsk (selon les données «*Statut sanitaire et épidémiologique ...* » 2006 - 2015) n'a pas démontré des relations directes avec les effets toxiques du brome, en raison du contenu de l'élément dans le sol.

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Le brome dans les milieux naturels de la région de Tomsk et évaluation de sa toxicité

Le brome, contrairement à d'autres éléments chimiques, reste l'un des moins étudiés à ce jour. Cependant, un grand nombre de travaux montrent qu'il peut être extrêmement toxique, exerçant un impact négatif sur les fonctions physiologiques importantes des organismes vivants et participant au développement et à la formation de certains types de maladies. L'objectif de cette thèse est d'établir les caractéristiques d'accumulation et de distribution du brome dans les composantes de l'environnement naturel de la région de Tomsk et de caractériser ses impacts toxicologiques sur la santé humaine et les écosystèmes selon le modèle USEtox. Elle est réalisée en combinant deux approches : les méthodes d'échantillonnage et les techniques de modélisation écologique. Dans le cadre de la thèse, la teneur en brome dans 2709 échantillons est considérée. La fiabilité du travail est garantie par un nombre statistiquement significatif d'échantillons, analysés par des méthodes modernes et hautement sensibles (INAA, ICP-MS, Analyse de fluorescence aux rayons X, Microscopie électronique à balayage) dans des laboratoires accrédités. De plus, pour la première fois, les facteurs de caractérisation d'impact du brome ont été calculés dans le modèle USEtox. Les résultats obtenus pourraient être utiles à l'avenir lors de l'évaluation des impacts environnementaux des produits chimiques et des risques associés pour les écosystèmes et la santé humaine, ainsi que pour le suivi géoécologique d'un territoire.

Mots clés : brome - environnement, études d'impact - géochimie de l'environnement - analyse du cycle de vie - évaluation de risque.

Bromine in the Natural Environments of the Tomsk Region and its Toxicity Assessment

Bromine in contrast to other, even less common chemical elements, still remains one of the least studied. However, a great number of works show that it can be extremely toxic, exerting a negative impact on important physiological functions of living organisms and participating in the development and formation of certain types of diseases. The objective of this thesis is to establish accumulation and distribution features of bromine in the components of the natural environment of the Tomsk region, and to characterize its human and ecotoxicological impacts according to the USEtox model. This is achieved by combining two approaches: sampling methods and ecological modeling technics. Within the framework of the thesis, the content of bromine in 2709 samples is considered. The reliability of the work is provided by a statistically significant number of samples, analyzed by modern highly sensitive analytical methods (INAA, ICP-MS, X-ray fluorescence analysis, scanning electron microscopy) in accredited laboratories. Also for the first time, characterization factors for bromine have been calculated within the USEtox model. The results obtained could be useful in the future when evaluating the environmental impacts of chemicals and the associated risks for ecosystems and human health as well as for geoecological monitoring of the territory.

Keywords: bromine - environmental impact analysis - environmental geochemistry -life cycle analysis - risk assessment.

Thèse réalisée en partenariat entre :

