
**ANTAGONISM OF HALOGENS IN THE SOIL AND WHEN
THEY ENTER PLANTS**

G.A. Konarbaeva¹, *Z. M. Sergazinova², V.V. Demin¹*¹Institute of soil science and agrochemistry Siberian Branch, Russian Academy of Science, Novosibirsk, Russia**²NJSC «Toraigyrov University», Pavlodar, Kazakhstan***mszarinam@mail.ru*

Summary

This article discusses the problem of halogen antagonism in soil and when they enter plants. Antagonism as one of the types of interaction of chemical elements in soil, including halogens, can lead to their deficiency or excess in plants. Antagonism is determined by the proximity of some properties of halogen anions, such as mobility of anions, solvation by the same number of water molecules, value of ionic radii, and can be a mechanism of their transport to plants.

Halogens (fluorine, chlorine, bromine and iodine) are among the most important trace elements necessary for living organisms. This review allows us to assume with confidence that due to the significant difference in concentrations of chlorine and iodine (the latter is orders of magnitude lower), it is unlikely that iodine can compete with chlorine in a serious way under the natural conditions. Antagonism between chloride and bromide anions is more probable. In our opinion, it is possible in soils located in the zone of industrial enterprises whose emissions contain bromine, and soils contaminated with bromine compounds at the level of chlorine. Considering the relatively low content of bromine and iodine in soils, especially iodine, it is difficult to talk about their antagonism in soils and plants.

As for fluorine, its content in soil compared with other halogens is maximum (about 200-500 mg/kg). It should be considered that fluorine differs from other halogens in a number of physicochemical properties and antagonism between them may be somewhat difficult.

Keywords: *halogens (fluorine, chlorine, bromine, iodine), antagonism, soil, plants.*

Introduction. Halogens – fluorine, chlorine, bromine and iodine play an important role in the life of living organisms, so their study should be detailed and versatile. Fluorine is a part of bone tissue and tooth enamel [1-2], chlorine activates some enzymes, maintains osmotic balance in the cells of living organisms, and participates in the digestive process in the form of hydrochloric acid [3-4]. Until recently, the role of bromine was somewhat uncertain, so it was attributed to conditionally essential elements [1,5]. But since 2014, after the publication of the work of American researchers, it has been classified as a group of vital elements, since without bromine, type IV collagen molecules, which play an important role in preserving the integrity of epithelial and endothelial cell membranes, cannot bind to each other properly to form a structural protein of connective tissue, which can lead to disruption of its development [6]. Iodine regulates the rate of metabolism in living organisms, and this process is associated with thyroid hormones, thyroxine and triiodothyronine. The composition of these hormones includes iodine, and not one element can replace its physiological function in them [7-8]. All this indicates that halogens are active participants in the process of forming the food chain:

atmosphere - soil – natural waters – plants – animals – man.

While studying halogens in natural objects of Western Siberia (soils, waters and plants), we decided to pay attention to such a problem as the antagonism of halogens, which can manifest itself between them both in the soil and when they enter plants. The antagonism of halogens as one of the types of interaction between chemical elements plays an important role in the life of plants, in their absorption of halogens and in the metabolic processes occurring in them. It is based on the significant similarity and difference of a number of their properties and can lead to their deficiency or excess when entering plants from the soil.

In natural conditions, there is practically no pure salinization by one of the halogens: they are always present together in the soil, so antagonism between them is quite possible. As for plants, they simultaneously absorb various halogen anions from the substrate. In this case, the interaction of similarly charged ions can be antagonistic [9].

Materials and methods. *Antagonism of halogens in soils.* The antagonism of halogens in the soil is controlled by the cumulative interaction

of the physicochemical properties of the elements themselves and the soils, which affect the processes of their absorption, consolidation and loss.

It is obvious that in different types of soils, the antagonism of halogens depends on a number of factors, such as their content in the soil profile, ion mobility, chemical activity of halogens and a tendency to valence variability, the reaction of the soil environment, the enrichment of the soil with organic matter.

The antagonism of halogens is also influenced by the gross content of halogens (Table 1). The huge difference in the concentrations of chlorine and iodine in soils (the latter is smaller by orders of magnitude) allows us to speak with confidence about the very low probability that iodine can seriously compete with chlorine. So in natural conditions, at least in most soils of Western Siberia, iodine can hardly be considered as an antagonist to chlorine.

According to experimental data, the main competitor of the chloride anion in soils is the bromide anion, as well as there is an antagonism between bromine and iodine and between fluorine and iodine when they enter plants, but the reasons why this happens in all cases are different.

Table 1. Limits of fluctuations of the gross content of halogens in soils of the south of Western Siberia in mg/kg.

The soil	F	Cl	Br	J
Sod-podzolic	210.0-270.8	25.2-91.0	0-2.8	0-2.4
Gray forest	220.4-290.7	48.3-55.6	1.2-3.6	0.3-4.7
Chernozems	389.6-440.9	22.0-40.6	1.7-14.0	0.1-6.7
Chestnut	200.1-271.4	34.6-44.4	1.3-3.3	0-2.6
Salt licks	250.0-550.0	152.2-221.3	1.8-33.3	1.8-19.7
Salt marshes	656.0-980.0	109.7-1089.6	11.3-59.4	4.4-35.4
Meadow, swamp	-	-	1.3-42.1	0.7-13.2

Consider the possibility of antagonism in different types of soils. The objects of the study were the soils of the south of Western Siberia, the content of halogens in which are given below [10, 11]. In automorphic soils,

such as Cambisols, Luvisols, Phaeozems, Chernozems, Kastanozems (hereinafter the names of soils are given according to ISSS 2014), the content of gross fluorine is below the permissible value (500 mg/

kg), in salt marshes (Solonetz) at the level of the permissible value and only in salt marshes (Solonchaks) its content is critical, almost 1000 mg/kg. The content of the water-soluble form is evaluated according to the following criteria: MPC is 10 mg/kg [12], the permissible level is 0-10, the critical level is 10-30 mg/kg [13]. The most commonly determined concentrations are from 0.43 to 8.23 mg/kg and only in salt marshes of 14.0 mg/kg or more of fluorine.

The total chlorine content in automorphic soils varies in the range from 25 to 51 mg/kg, water-soluble form - from 18.8 to 46 mg/kg. In intrazonal soils, respectively, from 110 to 1115 mg/kg and from 90 to 1035 mg/kg. The total chlorine content in Kursk chernozem (Haplic Chernozem), taken as a standard, is 70 mg/kg. State standards for the content of water-soluble chlorine have not been developed.

The total bromine content in automorphic soils (Luvisols, Phaeozems, Chernozems, Kastanozems) varies within 1.5–7.0 mg/kg, water-soluble form from 0.1 to 3.25 mg/kg; in intrazonal soils, respectively, from 7.0 to 54.0 mg/kg and 2.0 and 33.0 mg/kg. There are no state standards for bromine content in soils.

The content of gross iodine in automorphic soils is from 0.23 to 6.40 mg/kg, the water-soluble form is from traces to 0.1 mg/kg, in intrazonal soils (Gleysols, Solonezes, Solonchaks) – respectively from 2.1 to 18.7 mg/kg (gross content) and (0.05–17.8 mg/kg) the water-soluble form. There are no state standards for iodine content in soils. According to Kovalsky's gradations [14], the gross iodine content in soils up to 5.0 is insufficient, 5.0 – 40.0 is normal and more than 40 mg/kg is excessive.

Antagonism of halogens in plants. The rate of ion absorption by roots growing in the soil is determined by the interaction of both soil factors and plant-dependent factors. Since the mobility of ions decreases with an increase in the concentration of solutions [15], such a phenomenon can

affect the rate of movement of halogens in soil solutions. Therefore, even a slight difference in the values of ion mobility, according to our assumption, can affect the rate of their migration in soils. Of the other physicochemical properties of halogens of interest to the problem of halogen antagonism, it is worth recalling the existence of a calcium geochemical barrier for the fluoride anion due to the low solubility of CaF_2 (2-8 mg/L). The higher solubility of the most common chlorine, bromine and iodine salts in the soil excludes the occurrence of physico-chemical barriers in the hypergenesis zone, with the exception of evaporative in arid landscapes, where the accumulation of chlorine, bromine and iodine occurs. In relation to iodine, it plays a lesser role. At the same time, it should be noted that bromine and iodine are actively absorbed by organic matter, while iodine is even more energetic, which contributes to their concentration in humus horizons [16–17].

Obviously, the priority absorption of a certain halogen will be influenced not only by its increased content in the soil, but also by the chemical composition of the soil substrate as a whole.

According to Wallace [18], antagonism between cations or anions can lead to their deficiency in plants. According to Bitutsky [4], competition between elements can arise already at the stage of their physico-chemical adsorption by cell walls, while the bond strength varies greatly from the nature of ions and their concentration in the medium. Therefore, the study of the interaction of halogens when entering plants from the soil, as well as in the plants themselves, is of great interest.

Obviously, it is more logical to consider the competitiveness of bromide and iodide anions when they enter plants in relation to fluoride and chloride anions, the gross content of which in soils is orders of magnitude greater than bromine and iodine.

The degree of antagonism between halogens and the rate of their absorption by plants was investigated in great detail by Portyanko [19]. The essence of his experiments was that young sprouts were immersed successively in solutions of halogen analogues in various combinations. Sodium salts of all halogens of 0.001% concentration were used. The roots of plants pretreated with fluoride absorbed 25% iodine, 50% chlorine and 64% bromine compared to the control variant. Treatment of plants with iodine limited the intake of fluorine to 42%, chlorine to 53%, bromine to 64%. Bromine treatment limited the intake of fluorine to 48%, chlorine to 83%, iodine to 75%.

Plants that were not previously exposed to halogens served as controls in the experiments. It follows from the results obtained that bromine and chlorine are the strongest competitors, since it is the bromine treatment that limits the intake of chlorine into plants to 83%.

Results and discussion. The analysis of the obtained results suggests that the antagonism of halogens in the soil is quite possible. It is most likely between fluorine and chlorine in relation to bromine and iodine, as well as between chlorine and bromine, chlorine and iodine.

In chernozems, antagonism between bromine and iodine is quite possible in the upper humus horizons of the soil, since a sufficiently high content of organic matter in them plays a priority role in the accumulation of iodine, as well as bromine [15-16]. As a result, antagonism may arise between them for fixing in the soil. Antagonism between fluorine and chlorine is unlikely, since these halogens differ significantly in their behavior in soils and in their physico-chemical properties.

In sod-podzolic, gray forest and chestnut (Retisols, Luvisols, Phaeozems, Kastanozems) soils, the manifestation of antagonism between halogens is possible, but this process may be weakly manifested.

This situation, in our opinion, may be due to the fact that these soils are characterized by a washing and periodically washing water regime, which, taking into account the good solubility of most chlorine, bromine and iodine salts, do not contribute to their accumulation, and hence possible antagonism.

In chestnut soils of Kastanozems, the content of chlorine and especially bromine and iodine is very insignificant and even some moisture deficiency characteristic of these soils cannot allow them to be bright antagonists.

Antagonism between fluorine and the other three halogens in sod-podzolic, gray forest and chestnut soils is unlikely due to the significant content of fluorine. In order to confirm or refute our assumptions, experimental data are needed, which we plan to do in the near future.

Antagonism of halogens in plants. Fluorine and chlorine. In the literature, the fluoride anion is not considered as a serious competitor to the chloride anion when entering plants. Most fluorides are slightly soluble, therefore, they are mainly in the bound state in the soil, unlike chlorides, for which the ionic state is more characteristic due to the high solubility of their compounds. A comparison of the mobility indices of the fluoride anion - ($5.74 \times 10^4 \text{ m}^2 \text{ cm}^{-1} \text{ B}^{-1}$) and the chloride anion - ($7.91 \times 10^4 \text{ m}^2 \text{ cm}^{-1} \text{ In}^{-1}$) also indicates that the former is not in favor. Further, according to Kovalevsky [19], fluorine at high concentrations in the soil is a barrier element, and chlorine belongs to the barrier-free group, which also gives it priority. And finally, fluorine is always monovalent, while chlorine, whose valence varies from -1 to + 7, has a pronounced ability to oxidize and reduce, which undoubtedly plays a role in the processes occurring in the soil. In addition, the fluoride anion is characterized by a greater tendency to form complex compounds [21]. The stability of halide complexes, as a rule, decreases in

the series $F > Cl > Br > I$ [22], therefore many fluoride complexes are stable, do not lyophilize and weakly dissociate.

In addition to the difference in the mobility of fluoride and chloride anions, the hydration of water molecules can also affect the process of their entry into plants. The primary hydrate shell of halogens in aqueous solution contains four water molecules for fluorine and one for each of the other halogens [23]. The role of the diameter of the hydrated ion affects, according to Sutcliffe [24], the rate of entry of each individual ion. For this reason, monovalent ions are absorbed faster than two and multivalent ones. Based on this, we believe that the fluoride anion, solvated by four water molecules, has a larger size in space compared to the chloride anion, therefore it should move slower and be absorbed by plants less actively. The latter can serve as an additional hindering factor in the competition of fluorine and chlorine.

If fluorine and chlorine are considered from the standpoint of the need for plants, then chlorine is considered an indispensable element because of its specific role in photosynthesis reactions, in nitrogen and energy exchanges. Therefore, it is no coincidence that chlorine is in a group of seven elements (Fe, Mn, Zn, Cu, Mo, B and Cl), indisputably necessary for plants [4]. Fluorine does not yet belong to the elements necessary for plants, at least so far there is no consensus on this. According to Kabata-Pendias, the availability of fluorine to plants usually does not depend on its total content or the number of soluble forms [25]. So, taking into account the selectivity that is characteristic of plants in the processes of their absorption of various elements [23, 26], we can assume their preference for chlorine.

Chlorine and iodine. The few literature sources regarding the competitive ability of chloride and iodide anions indicate that the presence of chlorine in increased amounts delays the intake of iodine [27-

28]. Moreover, Nazarova [28] cites positive results of the use of antagonism between chlorine and iodine in order to increase the salt resistance of cotton through the use of pretreatment with iodine.

At the same time, another, opposite point of view is presented in the literature, according to which the iodide anion inhibits the entry of chloride anion into plants. This point of view is supported by Ilyin [27], who believes that the absorption of the chloride anion is more hindered by the iodide anion than by the nitrate or sulfate anions.

These contradictions can be explained by referring to the experiments [19], from which it follows that iodine is concentrated in the root bark almost three times more (63.2%) than chlorine (21.2%). So iodine, dominating the absorption of plants in the roots, can prevent the entry of chlorine.

According to [24], the absorption of chloride by plants decreases in the presence of not only iodine, but also bromine, and at the same time remains unchanged or even increases in the presence of nitrates or phosphates. At the same time, as shown by Nazarova [28], the antagonistic activity of iodine ions in relation to chlorine is several tens of times stronger than that of chlorine ions to iodine. As a result, despite the impressive predominance of chlorine concentration over iodine in the nutrient medium, the intake of chlorine into cotton seedlings decreased by 34-40%. According to the author, iodine has the ability to occupy active centers faster than chlorine. But it is impossible to explain this only by the difference in the mobility of anions, which is approximately the same for iodine and for chlorine and is $7.97 \times 10^4 \text{ m}^2\text{cm}^{-1}\text{B}^{-1}$ for iodine and $7.91 \times 10^4 \text{ m}^2\text{cm}^{-1}\text{B}^{-1}$ for chlorine. Churbanov [29] believes that the atomic mass plays a significant role in the antagonism between chlorine and iodine, which is more than three times larger in iodine (126.9) than in chlorine (35.45).

In our opinion, the antagonism between these halogens is facilitated by

the similarity of parameters such as ion mobility, solvation by a single water molecule and, possibly, biological features of plants, some species of which have a selective feature to absorb and accumulate iodine under comparable conditions [30]. It can also be suggested that iodine, having a larger ionic radius, inhibits the movement of the chloride anion.

But in any case, the concentration of iodine in plants is significantly lower than chlorine. But all these factors, in our opinion, are leveled in comparison with the content of halogens in the soil. The huge difference in the concentrations of chlorine and iodine (the latter is smaller by orders of magnitude) suggests a very low probability that iodine can seriously compete with chlorine. So in natural conditions, it is hardly possible to consider iodine as an antagonist to chlorine.

Chlorine and bromine. There is another opinion in the literature regarding chlorine antagonists. The main competitor of the chloride anion in soils when entering plants can only be the bromide anion. Experimentally, it was found that the absorption of chlorine by barley roots is not affected in any way by the presence of fluorides and iodides [31]. They noted only the effect of bromides.

A study on living roots using labeled atoms revealed that the main competitor for the bromide anion, which is a substrate, is the chloride anion [32].

Much later studies [33] devoted to the kinetics of competitive inhibition of a number of anions on the roots of wheat, barley and rye also showed the presence of inhibition of the transport of chlorine by bromine and bromine by chlorine and the absence of it in nitrate, sulfate and phosphate anions in relation to those.

Other researchers hold a similar view on the possibility of partial replacement of the chlorine needed by plants with bromine, the excess of which is toxic to them [25]. The experiments conducted by Portyanko

[19] also indicate a serious antagonism between chlorine and bromine: treatment of plant roots with 0.001% sodium bromide solution limited the intake of chlorine by 83%, which is the highest indicator in his experiments.

It is obvious that the antagonism in this case is due to the proximity of some properties of these anions, such as mobility, solvation by the same number of water molecules, the close magnitude of ionic radii (Br-0.195 nm; Cl-0.181 nm) and may be a similar mechanism of their transport to plants.

In addition, as Wallace established [18], the intensity of bromine anion intake, depending on the concentration in the solution, is linear, which means that a tenfold increase in the external concentration also leads to a tenfold increase in bromine intake into plants. The discovered direct dependence of incoming bromine in plants can play a certain role in the competition of bromine and chlorine in the processes of their transport to plants.

However, it should be noted that some of these data were obtained using KBr solution, as in Wallace [18], or bromine isotopes, as in Epstein and co-author [32]. We have not found evidence of the dominance of bromine over chlorine in plants under natural soil conditions as a result of their antagonism. Moreover, comparing the data on water-soluble forms of bromine (from trace amounts up to 3 mg/kg) and chlorine (18.8–54.9 mg/kg), the most accessible to plants found by us in the soils of Western Siberia and used in agriculture, we saw that the concentration of chlorine is one or two orders of magnitude higher, therefore, only chlorine can seriously compete with bromine when they enter plants. The implementation of the opposite option, in our opinion, can occur only in soils located in the zone of industrial enterprises, in the emissions of which bromine compounds are present, and contaminated with it at the level of chlorine or at least close to it.

The need for chlorine in plant nutrition has long been established. At the same time, some new aspects of the role of chlorine in this process are also discussed in the literature. Novak and co-author [33] made several assumptions: firstly, chlorine in a cell can perform an energy-saving function; secondly, plants in whose cells the storage vacuole has a relatively large size can respond positively to a relatively high chlorine content in the composition of mineral nutrition; and last, in the presence of chlorine, it will be more active synthesis of neutral organic substances. All this can contribute to the priority absorption of chlorine by plants. Similar studies regarding the role of bromine in plant nutrition are not yet available. Thus, in barley roots, the absorption of Cl⁻ is not affected in any way by the presence of other halide anions, F and I, although Br⁻ competitively suppresses this absorption [31].

Bromine and iodine. There is also antagonism between bromine and iodine when they enter plants, as follows from the experiments of Portyanko [19]. Pretreatment of the roots with bromine limits the intake of iodine to 75%, and in reverse order – to 64%. However, in natural conditions, attention is not paid to the antagonism of bromine and iodine due to their low content in soils. Perhaps for the same reason, there are no model experiments, although in soils of reduced relief elements in the south of Western Siberia, where the bromine content is noticeably higher than in zonal soils, it is worth paying attention to.

Bromine is a vital element, but in excess amounts it can have a harmful effect on all living organisms. Bromine can be very toxic to plants, since it is able to replace the chlorine necessary for them, as well as affect changes in the permeability of cell membranes [34-35]. According to [36], the increasing iodine deficiency observed today in many countries is associated with the accumulation of bromine in the environment. Bromine is one of the

strongest competitors of iodine for the active centers of enzymes [1] and is able to prevent its absorption [37].

Accumulating in plant cells, the element changes its forms of location: instead of inorganic salts found in soils and waters, it occurs in plants in the form of complex organic compounds [16].

The biological effect of bromine is twofold: on the one hand, the element is essential, on the other, it can be toxic.

Fluorine and iodine. The experiments of Portyanko [19] revealed a rather noticeable competition of fluorine and iodine when entering plants. When pretreating plant roots with fluoride, only 25% of iodine is absorbed by them, and when plants are treated with iodine, 42% of fluoride is absorbed by them. In our opinion, the blocking of iodine intake by fluorine in plants in this experiment can be explained as follows. Since the roots of plants were initially impregnated with fluorine, iodine could not simply compete with fluorine due to the large difference in chemical activity, which results in a very low percentage of its absorption. However, it is impossible to say unequivocally whether this is the case in reality. Probably, the degree of antagonism between fluorine and iodine would be different with their simultaneous application. The more active absorption of fluorine can be explained by relying on the chemical properties of halogens, primarily their activity. Fluorine displaces iodine from the roots according to the fact that in the F – Cl – Br – I series, the total energy released during the transition of its atom from the usual state to the hydrated one decreases, so each halide is able to displace all its halogens from their compounds to the right.

At the same time, the question arises, why did fluorine not completely displace iodine from the roots of plants, with which they were pretreated? It would seem that a very significant difference in their chemical activity should contribute to this, but the

plants absorbed a little less than half of the fluoride introduced. It is obvious that part of the fluorine could be absorbed by the roots of plants due to the insufficiency of iodine for them, the other part due to the high chemical activity of fluorine can be bound as a result of various metabolic reactions. The impossibility of complete displacement of iodine by fluorine from the roots, apparently, can be explained by the fact that part could have been absorbed by the roots of plants already quite firmly before fluorine began to act. Either iodine was already involved in the metabolic processes going on in the roots, and therefore fluorine could not be absorbed by 100%. It is worth noting that in all the experiments set by Portyanko, there was not a single case of a complete replacement of one halogen with another.

Conclusion. Obviously, the priority absorption of a certain halogen anion will be influenced not only by its increased content in the soil, primarily mobile forms, but also by the chemical composition of the soil substrate as a whole. In particular, the increased calcium content in the soil can inhibit the entry of halogens such as fluorine and chlorine due to the formation of fluorides and calcium chlorides and will not prevent the entry of bromine and iodine into plants. Calcium fluoride is a very poorly soluble compound, and the solubility of the anhydrous salt CaCl_2 is 2 and 3 times lower than the solubility of calcium bromide and iodide, respectively.

In addition, it is known that the number of individual ions absorbed from a complex nutrient solution is largely determined not so much by the absolute concentration as by the ratios between these ions in the nutrient solution [38]. In this case, based on our results on the water-soluble form of halogens in the soils of the south of Western Siberia, we can conclude that chlorine predominates not only in absolute content, but also in relation to other halogens.

The competitive ability when they enter plants will undoubtedly be influenced by the reaction of the environment. For example, in conditions of acidic reaction of the soil environment, when the intensity of bromine and iodine migration dominates the accumulation process, their influx to the root system will be weakened, while in alkaline conditions it will significantly increase.

Udovenko's experiments [9] showed a decrease in the absorption intensity of chlorine labeled with the ^{36}Cl radioisotope in the presence of a number of trace elements, such as boron and molybdenum. In this case, if the soil is enriched with these microelements, in particular boron, the intensity of chlorine absorption by plants should decrease. Since the vast territory of the south of Western Siberia, according to studies [39], is a zone of boron salinization, the situation with the influence of boron can be realized in this territory. As for molybdenum, it can be assumed with a high degree of probability that it will not be able to compete with chlorine and affect the intensity of its absorption by plants. This assumption is due to its relatively low content in the soils of the south of Western Siberia. In general, in the south of Western Siberia, the concentration of molybdenum in soils is 3.5 mg/kg [39], in the background area in Southern Vasyugan -2.9 mg/kg [41]. According to our data, in loess-like loams, the most common soil-forming rocks of the Ob-Irtysh interfluvium are 4.7 mg/kg [4].

Thus, selectivity in the absorption of certain macro- and microelements from the soil, characteristic of plants, contributes to their absorption of certain elements in a certain quantitative ratio. At the same time, as mentioned earlier, the issue of the antagonism of halogens to the soil and when they enter plants has been studied extremely poorly.

The absence in the literature of studies of the conjugate study of different pairs of halogens for the same crops and natural

vegetation does not allow us to estimate their mass flow in the soil-plant system and calculate the optimal ratio. It has long been known that a violation of the correct ratio between individual chemical elements both in the external environment and in the human and animal bodies can be the cause of their increased morbidity. For example, some researchers admit that with the predominance of fluorine over iodine in the external environment, the intensity of the goiter endemia also changes in the direction of strengthening. Moreover, it was found that dental fluorosis occurs together with an increase in the thyroid gland [45].

To solve the problem of the ratio of chlorine and bromine, comprehensive studies of the bromine content in soils and plants, its effect on vegetation, as well as the development of all necessary regulatory documents regulating its content in natural objects are necessary.

A few words should be said that antagonism exists not only between halogens, but also between halogens and other elements. For example, pathology in the functioning of the thyroid gland is observed not only in provinces with a low iodine content, but according to Kowalski's research [45] depends on the cobalt content, as well as on the ratio of these elements in the geochemical environment. Moreover, the lack or excess of manganese inhibits the synthesis of iodized thyroid compounds. In tropical soils, iron oxides can reduce the mobilization of iodine and its availability to plants [45].

Thus, with regard to halogens necessary for the normal functioning of living organisms, there is still a lot of antagonism that has not been studied in the problem, which should be given serious attention.

References

1. Avcyn A.P., Zhavoronkov A.A., Rish M.A., Strochkova L.S. "Mikrojelementozy cheloveka [Human microelementoses]." *M.: Medicina*, (1991): 495 – (In Russian)

2. "Vrednye himicheskie veshhestva [Harmful chemicals]." *L.: Himija*, (1989): 592 – (In Russian)

3. Perel'man A.I. "Geohimija [Geochemistry]." *M.: Vysshaja shkola*, (1979): 422 – (In Russian)

4. Bitjuckij, N.P. "Mikrojelementy i rastenija [Trace elements and plants]." *SPb.: Izd-vo S-Peterb. un-ta*, (1999): 230 – (In Russian)

5. Bgatov A.V. "Biogennaja klassifikacija himicheskikh jelementov [Biogenic classification of chemical elements]" // *Filosofija nauki*, no 2 (6) (1999): 12-24 – (In Russian)

6. McCall S., Cummings C., Bhave G., Vanacore R., et. al. Bromine is an essential trace element for assembly of IV scaffolds in issue development and architecture // *Cell*. – 2014. – Vol. 157. – P. 1380-1392.

7. Mohnach, V.O. "Jod i problemy zhizni [Iodine and problems of life]." *L.: Nauka Leningrad. otd-nie*, (1974): 253 – (In Russian)

8. Mohnach, V.O. "Teoreticheskie osnovy biologicheskogo dejstvija galoidnyh soedinenij [Theoretical foundations of the biological action of halogen compounds]." *L.: Nauka. Leningr. otd-nie*, (1968): 297 – (In Russian)

9. Udovenko, G.V. "Soleustojchivost' kul'turnyh rastenij [Salt tolerance of cultivated plants]." *L.: Kolos*, (1977): 181 – (In Russian)

10. Konarbaeva G.A. "Galogeny v prirodnyh ob#ektah juga Zapadnoj Sibiri Avtoref. dis. na soiskanie uchenoj stepeni d.b.n. [Halogens in natural objects of the south of Western Siberia Abstract of the thesis. dis. for the degree of Doctor of Biological Sciences]." *Novosibirsk*, 2008: 33 – (In Russian)

11. Sergazinova, Z.M., Dupal, T.A., Litvinov, Ju. N., Erzhanov, N.T., Konarbaeva, G.A. "Vozdejstvie vybrosov aljuminievogo proizvodstva v Severnom Kazahstane na vidovuju strukturu i karakter nakoplenija ftora u melkih mlekopitajushhih [Impact of emissions of aluminum production in Northern Kazakhstan on the species structure and nature of fluorine accumulation in small mammals]." // *Principy jekologii.*, № 3. DOI: 10.15393/j1.art.2018.7902 (2018): 60–74. – (In Russian)

12. G.N.2.1.7.2041-06. "Predel'no dopustimye koncentracii (PDK) himicheskikh veshhestv v pochve [Maximum allowable concentrations (MPC) of chemicals in soil]." M., (2006): 15 – (In Russian)
13. "Sanitarnye normy dopustimyh koncentracij toksichnykh veshhestv v pochve [Sanitary standards for permissible concentrations of toxic substances in the soil]." SanPiN 42-126-4433-87. – (In Russian)
14. Koval'skij V.V. "Biologicheskaja rol' joda [The biological role of iodine]" // *Biologicheskaja rol' joda. Nauchnye trudy VASHNIL*. M.: Kolos, (1972): 3-32. – (In Russian)
15. Nekrasov B.V. "Osnovy obshhej himii [Fundamentals of General Chemistry]." M.: Himija, T.1, (1973): 270-296. – (In Russian)
16. Rozen B.Ja. "Geohimija broma i joda [Geochemistry of bromine and iodine]." M.: Nedra, (1970):132. – (In Russian)
17. Vinogradov A.P. "Geohimija redkih i rassejannykh himicheskikh jelementov v pochvah [Geochemistry of rare and trace elements in soils]." M.: Izd-vo AN SSSR, (1957): 234. – (In Russian)
18. Uolles A. "Pogloshhenie rastenijami pitatel'nyh veshhestv iz rastvorov [Plant uptake of nutrients from solutions]." M.: Kolos, (1966): 279. – (In Russian)
19. Portjanko V.F. "Antagonizm galogenov i ih pogloshhenie rastenijami iz okruzhajushhej sredy. Mikrojelementy v okruzhajushhej srede [Antagonism of halogens and their uptake by plants from the environment. Trace elements in the environment]." Kiev: Nauk. Dumka, (1980): 96-99. – (In Russian)
20. Kovalevskij A.L. "Biogeohimija rastenij [Plant biogeochemistry]." Novosibirsk: Nauka. Sib. otd., (1991): 294. – (In Russian)
21. Poling L., Poling P. "Himija [Chemistry]." M.: Mir, (1978): 683. – (In Russian)
22. Kotton F., Uilkinson Dzh. "Osnovy neorganicheskoj himii [Fundamentals of inorganic chemistry]." M.: Mir, (1979): 256. – (In Russian)
23. Klarkson D. "Transport ionov i struktura rastitel'noj kletki [Ion transport and plant cell structure]." – M.: Mir, (1978): 365.– (In Russian)
24. Satklif D.F. "Pogloshhenie mineral'nyh solej rastenijami [Absorption of mineral salts by plants]." M., (1964): 221. – (In Russian)
25. Kabata-Pendias A., Pendias H. "Mikrojelementy v pochvah i rastenijah [Trace elements in soils and plants]." M.: Mir, (1989): 439. – (In Russian)
26. Il'in V.B. "Jelementnyj himicheskij sostav rastenij Trace elements in soils and plants [Elemental chemical composition of plants]." Novosibirsk: Nauka, Sib. otd., (1985): 129. – (In Russian)
27. Katalymov M.V. "Problema joda v agrohimii [The problem of iodine in agricultural chemistry]" // *Agrohimija*, № 1 (1964): 69-81. – (In Russian)
28. Nazarova S.M. "Vlijanie joda na soleustojchivost' hlochatnika: Avtoref. disser. ... kand. biol. nauk [The effect of iodine on the salt tolerance of cotton: Abstract of the thesis. dissertation ... cand. biol. Sciences]." Tashkent, (1972): 20. – (In Russian)
29. Churbanov V.N. "Oprichinah snizhenija postuplenija joda v rastenija na izvestkovykh pochvah [On the reasons for the decrease in iodine intake in plants on calcareous soils]." // *Tr. Altajskogo s-h in-ta*, Vyp. 9 (1966): 53-63. – (In Russian)
30. Kashin V.K. "Jod v rastitel'nom pokrove agrolandshaftov Zabajkal'ja [Iodine in the vegetation cover of agricultural landscapes in Transbaikalia]." // *Agrohimija*, № 6 (1992): 86-93. – (In Russian)
31. Elzam O.E., Epstein E. Salt relations of to grass species differing in salt tolerance. II Kinetics of absorption of K, Na and Cl by their excised roots // *Agrochimica*. – 1969. – Vol. 13. – P. 196-206.
32. Jepshtejn Je., Hendriks S.B. "Pogloshhenie i peredvizhenie mineral'nyh pitatel'nyh veshhestv v kornjah rastenij [Absorption and movement of mineral nutrients in plant roots]." // *Dokl. inostr. uchenyh na Mezhdunar. konf. po mirnomu ispol'zovaniju atomnoj jenerгии*. M.: Izd-vo AN SSSR, (1956): 645. – (In Russian)
33. Novak V. A., Jakimov Ju. E. "Transport i vlijanie hlora na rost rastenij [Transport and effects of chlorine on plant growth]" // *Doklady*

- Akademii nauk SSSR, Tom 292, № 2 (1987): 508-512. – (In Russian)*
34. Kabata-Pendias, Trace Elements in Soils and Plants, Fourth Edition” // Taylor & Francis. – 2011. – 548 p.
35. Nazer I.K., Hallak A.B. Abu- Gharbieh, W.L. “Bromine residues in the soil and fruits of certain crops after soil fumigation with methyl bromide” // *Journal of Radio analytical Chemistry.* – 1982. – Vol. 74, – № 1. – P 113-116.
36. Vobesky M., Babicky A., Lener J. Effect of increased bromide intake on iodine excretion in rats // *Biological trace element research.* – 1996. – Vol. 55. – P. 215-219.
37. Pavelka S., Babicky A., Vobecky M., Lener J, Effect of high bromide levels in the organism on the biological half- life of iodine in the rat. // *Biological Trace Element Research.* 2001. – Vol. 82. – № 1-3. – P. 125-132.
38. Olsen C. The significance of concentration for the rate of ion absorption by higher plants in water culture // *Physiol. Plant.* – 1950. – № 3. – P 152-164.
39. Il'in V.B., Anikina A.P. “Oblast' bornogo zasolenija v Sibiri [The area of boron salinization in Siberia].” // *Jetjudy po biogeohimii agrohonii jelementov - biofilov.* Novosibirsk: Nauka, Sib. otd-nie, (1977): 38-47. – (In Russian)
40. “Jekogeohimija Zapadnoj Sibiri [Ecogeochemistry of Western Siberia]”: Tr. OIGGM. – Vyp. 824. Novosibirsk: Izd-vo SO RAN, NIC OIGGM, (1996): 246. – (In Russian)
41. Rihvanov L.P., Sarnaev S.I., Jazikov E.G. Pochva kak deponirujushhaja sreda pri izuchenii tehnogenogo faktora vozdejstvija na prirodu [Soil as a deposit medium in the study of the technogenic factor of impact on nature] // *Problemy regional'noj jekologii.* Tomsk, Vyp. 3 (1994): 35-45. – (In Russian)
42. Il'in V.B., Syso A.I., Konarbaeva G.A. i dr. “Soderzhanie tjazhelyh metallov v pochvoobrazujushhijh porodah juga Zapadnoj Sibiri [The content of heavy metals in soil-forming rocks of the south of Western Siberia].” // *Pochvovedenie,* № 9 (2000): 1086-1090. – (In Russian)
43. Isaac A., Delphine W., Silvia C.R., Somanna S.N. et al. Prevalence and manifestations of water –born fluorosis among school children in Kaiwara village of India a preliminary study // *Asian Biomed.* – 2009. – №3. – P 1-4.
44. Koval'skij V.V., Blohina R.I. Geohimicheskaja jekologija jendemicheskogo zoba [Geochemical ecology of endemic goiter] // *Tr. biogeohim. lab. M.: Nauka T. 13 (1974): 191-216. – (In Russian)*
45. Balzer L.B., Schulz K., Birkel C. and Biester H. Iron oxides control sorption and mobilisation of iodine in a tropical rainforest catchment // *Soil Discuss.* – 2020. DOI:10.5194/ soil-2020-20.

Список использованных источников

1. Авцын А.П., Жаворонков А.А., Риш М.А., Строчкова Л. С. Микроэлементозы человека. – М.: Медицина, 1991. – 495 с.
2. Вредные химические вещества. – Л.: Химия, 1989. – 592 с.
3. Перельман А. И. Геохимия. – М.: Высшая школа, 1979. – 422 с.
4. Битюцкий Н.П. Микроэлементы и растения. – СПб.: Изд-во С-Петербур. ун-та, 1999. – 230 с.
5. Бгатов А.В. Биогенная классификация химических элементов // *Философия науки.* – 1999. – №2 (6). – С. 12-24.
6. McCall S., Cummings C., Bhave G., Vanacore R., et. al. Bromine is an essential trace element for assembly of IV scaffolds in issue development and architecture // *Cell.* – 2014. – Vol. 157. – P. 1380-1392.
7. Мохнач В.О. Йод и проблемы жизни. – Л.: Наука Ленинград. отд-ние, 1974. – 253 с.
8. Мохнач В.О. Теоретические основы биологического действия галоидных соединений. – Л.: Наука. Ленингр. отд-ние, 1968. – 297 с.
9. Удовенко Г.В. Солеустойчивость культурных растений. – Л.: Колос, 1977. – С. 181.
10. Конарбаева Г. А. Галогены в природных объектах юга Западной Сибири Автореф. дис. на соискание ученой степени д.б.н. – Новосибирск, 2008. – 33 с.
11. Сергазинова З.М., Дунал Т.А., Литвинов Ю.Н., Ержанов Н.Т., Конарбаева Г.А. Воздействие выбросов алюминиевого произ-

- водства в Северном Казахстане на видовую структуру и характер накопления фтора у мелких млекопитающих // *Принципы экологии*. – 2018. – № 3. С. 60–74. DOI: 10.15393/j1.art.2018.7902
12. Г.Н.2.1.7.2041-06. Предельно допустимые концентрации (ПДК) химических веществ в почве. – М., 2006. 15 с.
13. Санитарные нормы допустимых концентраций токсичных веществ в почве. СанПиН 42-126-4433-87.
14. Ковальский В. В. Биологическая роль йода // *Биологическая роль йода. Научные труды ВАСХНИЛ*. – М.: Колос, 1972. – С.3-32.
15. Некрасов Б.В. Основы общей химии. – М.: Химия, 1973. – Т.1. – С. 270-296.
16. Розен Б. Я. Геохимия брома и йода. – М.: Недра, 1970. – 132 с.
17. Виноградов А.П. Геохимия редких и рассеянных химических элементов в почвах. – М.: Изд-во АН СССР, 1957. – 234 с.
18. Уоллес А. Поглощение растениями питательных веществ из растворов. – М.: Колос, 1966. – 279 с.
19. Портянко В.Ф. Антагонизм галогенов и их поглощение растениями из окружающей среды. Микроэлементы в окружающей среде. – Киев: Наук. Думка, 1980. – С. 96-99.
20. Ковалевский А.Л. Биогеохимия растений. – Новосибирск: Наука. Сиб. отд. 1991. – 294 с.
21. Полинг Л., Полинг П. Химия. – М.: Мир, 1978. – 683 с.
22. Коттон Ф., Уилкинсон Дж. Основы неорганической химии. – М.: Мир, 1979. – 256 с.
23. Кларксон Д. Транспорт ионов и структура растительной клетки. – М.: Мир, 1978. – 365 с.
24. Сатклиф Д.Ф. Поглощение минеральных солей растениями. – М., 1964. – 221с.
25. Кабата-Пендиас А., Пендиас Х. Микроэлементы в почвах и растениях. – М.: Мир, 1989. – 439 с.
26. Ильин В.Б. Элементный химический состав растений. – Новосибирск: Наука, Сиб. отд., 1985. – 129 с.
27. Катальмов М.В. Проблема йода в агрохимии // *Агрохимия*. – 1964. – № 1. – С. 69-81.
28. Назарова С.М. Влияние йода на устойчивость хлопчатника: Автореф. диссер. ... канд. биол. наук. – Ташкент, 1972. – 20 с.
29. Чурбанов В.Н. О причинах снижения поступления йода в растения на известковых почвах. // *Тр. Алтайского с-х ин-та*. – 1966. – Вып. 9. – С. 53-63.
30. Кашин В.К. Йод в растительном покрове агроландшафтов Забайкалья // *Агрохимия*. – 1992. – № 6. – С. 86-93.
31. Elzam O. E., Epstein E. Salt relations of to grass species differing in salt tolerance. II Kinetics of absorption of K, Na and Cl by their excised roots // *Agrochimica*. – 1969. – Vol. 13. – P. 196-206.
32. Эпштейн Э., Хендрикс С.Б. Поглощение и передвижение минеральных питательных веществ в корнях растений // *Докл. иностр. ученых на Междунар. конф. по мирному использованию атомной энергии*. – М.: Изд-во АН СССР, 1956. – С. 645.
33. Новак В.А., Якимов Ю.Е. Транспорт и влияние хлора на рост растений // *Доклады Академии наук СССР*, 1987. – Том 292. – № 2. – С.508-512.
34. Кабата-Пендиас, Trace Elements in Soils and Plants, Fourth Edition // Taylor & Francis. – 2011. – 548 p.
35. Nazer I.K., Hallak A.B. Abu- Gharbieh W.L. Bromine residues in the soil and fruits of certain crops after soil fumigation with methyl bromide // *Journal of Radio analytical Chemistry*. – 1982. – Vol. 74, – № 1. – P 113-116.
36. Vobesky M., Babicky A., Lener J. Effect of increased bromide intake on iodine excretion in rats // *Biological trace element research*. – 1996. – Vol. 55. – P. 215-219.
37. Pavelka S., Babicky A., Vobecky M., Lener J, Effect of high bromide levels in the organism on the biological half- life of iodine in the rat. // *Biological Trace Element Research*. 2001. – Vol. 82. – № 1-3. – P. 125-132.
38. Olsen C. The significance of concentration for the rate of ion absorption by higher plants in water culture // *Physiol. Plant*. – 1950. – № 3. – P 152-164.

39. Ильин В.Б., Аникина А.П. *Область борного засоления в Сибири // Этюды по биогеохимии агрохимии элементов - биофиллов. – Новосибирск: Наука, Сиб. отд-ние, 1977. – С. 38-47.*

40. *Экогеохимия Западной Сибири: Тр. ОИГГМ. – Вып. 824. – Новосибирск: Изд-во СО РАН, НИЦ ОИГГМ, 1996. – 246 с.*

41. Рихванов Л.П., Сарнаев С.И., Язиков Е.Г. *Почва как депонирующая среда при изучении техногенного фактора воздействия на природу // Проблемы региональной экологии. – Томск, 1994. – Вып. 3. – С. 35-45.*

42. Ильин В.Б., Сысо А.И., Конарбаева Г.А. и др. *Содержание тяжелых металлов в почвообразующих породах юга Западной Сибири // Почвоведение. – 2000. – № 9. – С. 1086-1090.*

43. Isaac A., Delphine W., Silvia C.R., Somanna S.N. et al. *Prevalence and manifestations of water-borne fluorosis among school children in Kaiwara village of India^ a preliminary study // Asian Biomed. – 2009. – №3. – P 1-4.*

44. Ковальский В. В., Блохина Р.И. *Геохимическая экология эндемического зоба // Тр. биогеохим. лаб. – М.: Наука, 1974. – Т. 13. – С. 191-216.*

45. Balzer L.B., Schulz K., Birkel C. and Biester H. *Iron oxides control sorption and mobilisation of iodine in a tropical rainforest catchment // Soil Discuss. – 2020. DOI:10.5194/soil-2020-20.*

Material received on 25.05.23

Топырақта галогендердің және олардың өсімдіктерге ену кезіндегі антагонизмі

Аңдатпа

Бұл мақалада топырақтағы галогендердің антагонизмі және олардың өсімдіктерге ену кезіндегі мәселесі талқыланады. Антагонизм топырақтағы химиялық элементтердің, соның ішінде галогендердің өзара әрекеттесуінің бір түрі ретінде олардың өсімдіктерде тапшылығына немесе артық болуына әкелуі мүмкін. Өйткені, антагонизм галоген аниондарының кейбір қасиеттерінің жақындығымен анықталады, мысалы,

ерігіштігі, иондық радиустардың мөлшері және оларды өсімдіктерге тасымалдау механизмі болуы мүмкін.

Галогендер (фтор, хлор, бром және йод) тірі организмдерге қажетті маңызды микроэлементтердің бірі болып табылады. Орындалған шолу хлор мен йод концентрациясының айтарлықтай айырмашылығына байланысты (соңғысы азырақ) табиғи жағдайда йод хлормен айтарлықтай бәсекелесуі екіталай екенін сенімді түрде көрсетеді. Хлорид пен бромид аниондары арасындағы антагонизм ықтималдығы жоғары. Біздің ойымызша, бұл шығарындыларында бром бар және топырақ хлор деңгейіндегі бром қосылыстарымен ластанған өнеркәсіптік кәсіпорындар аймағында орналасқан топырақтарда мүмкін. Топырақтағы бром мен йодтың, әсіресе йодтың салыстырмалы түрде төмен болуына байланысты олардың топырақтағы және сәйкесінше өсімдіктердегі антагонизмі туралы айту қиын.

Фторға келетін болсақ, оның басқа галогендермен салыстырғанда топырақтағы мөлшері максималды (шамамен 200-500 мг/кг). Фтордың бірқатар физика-химиялық қасиеттері бойынша басқа галогендерден ерекшеленетінін және олардың арасындағы антагонизм біршама қиын болуы мүмкін екенін есте ұстаған жөн.

сөздері: галогендер (фтор, хлор, бром, йод), антагонизм, топырақ, өсімдік.

Материал баспаға 25.05.23 түсті

Антагонизм галогенов в почве и при поступлении их в растения

Аннотация

В данной статье обсуждается проблема антагонизма галогенов в почве и при поступлении их в растения. Антагонизм как один из видов взаимодействия химических элементов в почве, в том числе и галогенов, может привести к их дефициту или избытку в растениях. Ведь антагонизм определяется близостью некоторых свойств анионов галогенов, таких как подвижность анионов, сольватированность одинаковым числом

молекул воды, величиной ионных радиусов и может быть механизмом их транспорта в растения.

Галогены (фтор, хлор, бром и йод) относятся к числу важнейших микроэлементов, необходимых для живых организмов. Выполненный обзор позволяет с уверенностью предположить, что из-за значительной разницы в концентрациях хлора и йода (последнего на порядки меньше) вряд ли йод в естественных условиях может составить серьезную конкуренцию хлору. Более вероятен антагонизм между хлорид- и бромид-анионами. По нашему мнению, это возможно в почвах, расположенных в зоне промышленных предприятий, в выбросах которых присутствует бром, и почвы загряз-

нены соединениями брома на уровне хлора. Ввиду относительно низкого содержания в почвах брома и йода, особенно йода, трудно говорить об их антагонизме в почвах и соответственно в растениях.

Что касается фтора, то его содержание в почве в сравнении с остальными галогенами максимальное (примерно 200-500 мг/кг). При этом следует иметь в виду, что фтор по целому ряду физико-химических свойств отличается от других галогенов и антагонизм между ними может быть несколько затруднен.

Ключевые слова: галогены (фтор, хлор, бром, йод), антагонизм, почва, растения.

Материал поступил в редакцию
25.05.2023