Overview and Dynamics of Iodine and Bromine in the Environment

1. Dynamics of iodine and bromine in soil-plant system

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Abstract

The authors have developed a practical radioactivation analytical method for the determination of I and Br concentrations. Most soils in Japan contain high levels or both elements (average values, I : 43 mg/kg dry wt., Br : 102 mg/kg dry wt.) except for paddy soils. The high concentrations are ascribed to the environmental conditions (wet and mild climate, acidic soils) that are conducive to the capture of both elements originating from the atmosphere. The contents of both elements in plants (aerial parts) are at a slightly higher level than the worldwide average, suggesting that both elements in soils occur in insoluble forms that cannot be easily absorbed by the plants. The very low concentrations of I and Br in paddy soils (average content, I : 1.8 mg/kg dry wt., Br : 5.3 mg/kg dry wt.) were attributed to rapid dissolution and leaching. Under flooded conditions, the dissolution ratios of both elements increased remarkably, especially, that of I increased by one thousand times along with the change of the chemical forms. Under the oxidizing conditions of non-flooded soil, IO_3- (oxidation no.5) accounted for 90% of the total I, a value comparable to that in rain water. Under the reducing flooded conditions, $^-$ (oxidation no.-1) accounted for 90%. The I content did not vary appreciably among plant species but was markedly different among plant organs. The average I content (mg/kg dry wt.) in the organs of various plants in Japan was: leaves, 0.46 > fruits, 0.14 > edible roots, 0.055 > seeds, 0.0039. Active intake of green vegetables for the prevention of goiter was suggested.

Discipline: Agricultural environment/Soils, fertilizers and plant nutrition
Additional key words: Chernobyl, chlorine, geochemical cycle, paddy field, soil solution

Introduction

Among the halogen elements, iodine (I), bromine (Br) and chlorine (Cl) exhibit similar chemical properties, and are known as triad elements. Each of them displays high chemical and physiological activities and exerts a significant effect on the life and growth of plants and animals. Since these elements occur usually in a water soluble chemical form and sometimes in a volatile chemical form, they can be easily transferred in the environment.

The content and dynamics of the triad elements (I, Br, Cl) vary considerably depending on the environmental conditions, and together

with those changes, deficiency and excess (toxicity) for plants and animals widely occur. Moreover, the deposition of artificial organic halogen compounds in the environment is associated with environmental pollution. Though they display many similarities, at the same time their content and dynamics in the environment are remarkably different, and they exert a physiological influence on plants and animals.

I is a component of thyroxine, the thyroid hormone, which is an essential nutrient for animals and humans[18]. Goiter due to I deficiency in food and water supply has been observed in humans and animals for thousands of years all over the world. Nowadays, in China, India and Africa, etc., two billion people in the world are suffering from this disease.

Since the intake of I by the Japanese is high due the consumption of a large amount of I-rich marine products such as kelp, very few reports on goiter in man have been published in Japan. On the other hand, goiter of cattle due to a deficiency of I presumably was reported at a high rate for calves delivered by grazing cows in the inland areas of Iwate Prefecture[13]. After seaweed powder was added to the maternal feed, the occurrence of this disease decreased remarkably.

Essentiality of I for higher plants has not been confirmed[14]. The toxicity of I to higher plants is stronger than that of Br and Cl, and "Reclamation-Akagare" disease of lowland rice grown on newly reclaimed paddy soils caused by excessive absorption of I is well-known[15-17].

On the other hand, along with the recent rapid development of the use of atomic energy, increasing attention is being paid to the exposure to radioiodine released from the nuclear facilities into the environment. During the accident which occurred at the nuclear power plant in Chernobyl, U.S.S.R., in 1986, the deposition of ^{131}I (half-life, 8 days) was the highest among all nuclides, as the level of ^{131}I was monitored almost every day during the early stage after the accident by a radiological surveillance network throughout Japan[41].

Furthermore, there is a current concern about the long-lived isotope ^{129}I (half-life, 1.6×10^7 years), which may be discharged into the atmosphere and sea from spent nuclear fuel reprocessing-plants and other facilities. Emphasis is placed on the need to monitor the radiation doses resulting from ^{129}I accumulation in the environment for a long time and to develop measures of control[4,5].

The essentiality of Br for plants and animals has still not been recognized[23,40]. However, since an excessive intake of Br by humans is harmful to their health, the maximum permissible limit of Br in food originating from agricultural chemicals such as methylbromide (MB), etc. has been established in many countries throughout the world[27,37]. The use of MB (CH_3Br) products with halons (CF_3Br, and CF_2BrCl) emitting Br atom which destroys the ozone layer is now being regulated internationally[1].

The formation of carcinogenic trihalomethanes such as $CHBrCl_2$, $CHBr_2Cl$, etc. increases with the rise in the bromide concentration in water when drinking water is produced from chlorinated inland water such as river water[3]. Therefore, the development of countermeasures to prevent environmental pollution originating from Br, including the atmosphere and the hydrosphere is necessary.

Analytical method for the determination of I, Br and Cl concentrations

The author developed a practical neutron activation analysis (NAA) method for the determination of the concentration of the triad elements in plants, soils, soil-solutions and rain water[33]. This method was used preferentially for studies on the dynamics of I and Br in the soil-plant system.

In the NAA, the radioactivity of the nuclides (isotopes) generated by the thermal neutron capture in the samples was measured. This

method shows a very high sensitivity, a high accuracy and reproducibility for the triad elements with low interferences in the differentiation of the triad elements due to the utilization of the differences in the radiation properties of the radionuclides[24].

Also, radioactive isotope tracers, [131]I (half-life, 8 days), [125]I (half-life, 60 days) and [77]Br (half-life, 57 hr) were often used for studies on the dynamics of I and Br in the soil-plant system[25]. These tracers are very useful to assay newly added I and Br and to differentiate them from the native ones in the soils.

Soil-plant system in the global geochemical cycle of I and Br

1) From sea water to the atmosphere

Average composition of the triad elements in various components of the environment is

Table 1. Average composition of the triad elements in water, air, terrestrial plants and soil

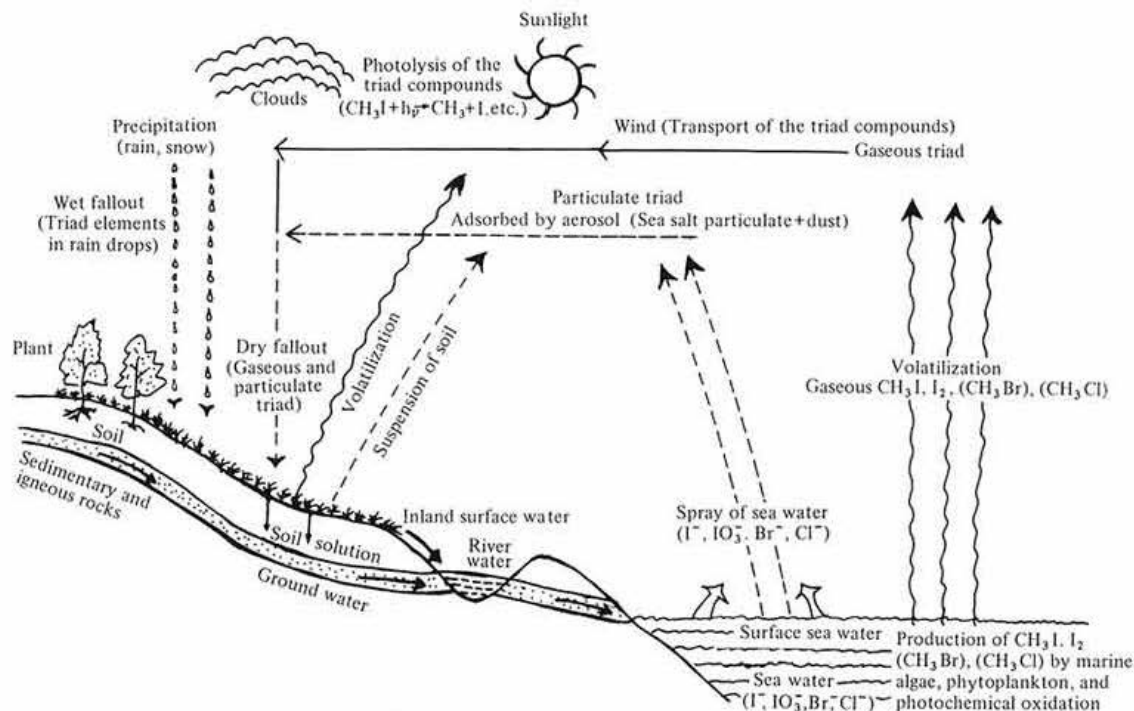|		I	Br	Cl
Sea water	mg/L	0.064 (1.0)	65 (1,016)	19,000 (296,875)
Air	$\mu g/m^3$	0.002 (1.0)	0.0044 (2.2)	3.5 (1,750)
Rain water	mg/L	0.0015 (1.0)	0.004 (2.7)	1.5 (1,000)
Ground water	mg/L	0.001 (1.0)	0.01 (10)	20 (20,000)
Terrestrial plants	mg/kg	0.42 (1.0)	15 (35.7)	2,000 (4,762)
Soil	mg/kg	5 (1.0)	5 (1.0)	100 (20)
Igneous rocks	mg/kg	0.5 (1.0)	2.5 (5.0)	130 (260)

Source: Bowen, H. J. M. (1966)[2].

Fig. 1. Geochemical cycle of triad elements (I, Br, Cl)

shown in Table 1. Sea water mainly supplies I and Br in soil and not the parent rocks of soils. Though both elements are easily eluviated during the weathering process of rocks due to their low resistance to weathering, the contents of both elements are much higher in soils than in parent rocks.

Geochemical cycle of the triad elements in the environment is shown in Fig. 1. I and Br in sea water move into the atmosphere as sea salt particles with Cl produced from bubbles bursting at the sea surface by the wave action. Another major route of transfer of I from the sea to the atmosphere, compared with Br and Cl, presumably is represented by the evaporation of volatile species mainly as methyliodide (CH_3I) generated from inorganic iodine (IO_3^- and I^-) by the biological processes of algae and phytoplankton and a small amount as I_2 by ultraviolet light and ozone in the sea surface water[9,19].

In this major additional route of I transfer, the concentration ratios of I to Br or Cl in the atmosphere are more than 100 times higher than the ratios in sea water.

2) From the atmosphere to the soil-plant system

I and Br in the atmosphere are transported onto land by the wind, fall on the soil-plant system of the earth surface and are deposited or adsorbed by them. There are three physicochemical forms of I and Br in the atmosphere, including the particulate form consisting of sea salt particles or dust, a gaseous organic and inorganic form, and a liquid form incorporated into rain drops or snow.

Concerning the physicochemical form of airborne ^{131}I emitted during the Chernobyl accident, it was reported[10] that particulate I accounted for 19%, gaseous inorganic I, I_2 for 5%, HOI for 6%, and gaseous organic I such as methyliodide (MI), etc. for 70%. Chemical forms of non-radioactive I are considered to

be almost the same as ^{131}I, and easily change depending on the environmental conditions[9]. For instance, MI can be easily decomposed into gaseous inorganic I of elemental iodine (I_2), HOI, etc. in the atmosphere by photolytic dissociation.

Among the chemical forms of ^{131}I in rain water, IO_3^- was the dominant form (94% of water soluble I), followed by I^- (4.4%)[41]. Chemical forms of ^{131}I in rain water also changed with the lapse of time in the reservoir[7,41]. Chemical forms of non-radioactive I examined at the same time showed almost similar values (%).

Deposition velocities of I on plants are very different depending the physicochemical forms. The deposition velocity of elemental I (I_2) is 100 times faster than that of MI[9], and thus, I_2 is deposited much more readily onto plants than MI. Almost no data are available about the deposition of I in rain water.

Fig. 2 shows the influence of rainfall on the ^{131}I deposition on wheat tops and soil during the Chernobyl nuclear reactor accident[41]. The deposition of ^{131}I on the wheat tops was mainly due to the dry deposition of gaseous and particulate ^{131}I in the air, and not to the wet deposition of ^{131}I in rainfall. On the other hand, deposition of ^{131}I onto the surface soil was due to the wet deposition of ^{131}I in rainfall. On days without rain, an increase in the concentration of ^{131}I in wheat tops and a decrease in the surface soil were recorded. When it rained, the concentration of ^{131}I in wheat tops tended to decrease while the concentration of ^{131}I in the surface soil increased. The concentration of ^{131}I in the surface soil decreased to 50% during the period from May 8 to May 10 under clear weather and at a high air temperature, presumably due to the volatilization of ^{131}I from the surface soil.

No data are available on the physicochemical forms of Br in the atmosphere and the deposition of Br onto plants and soils.
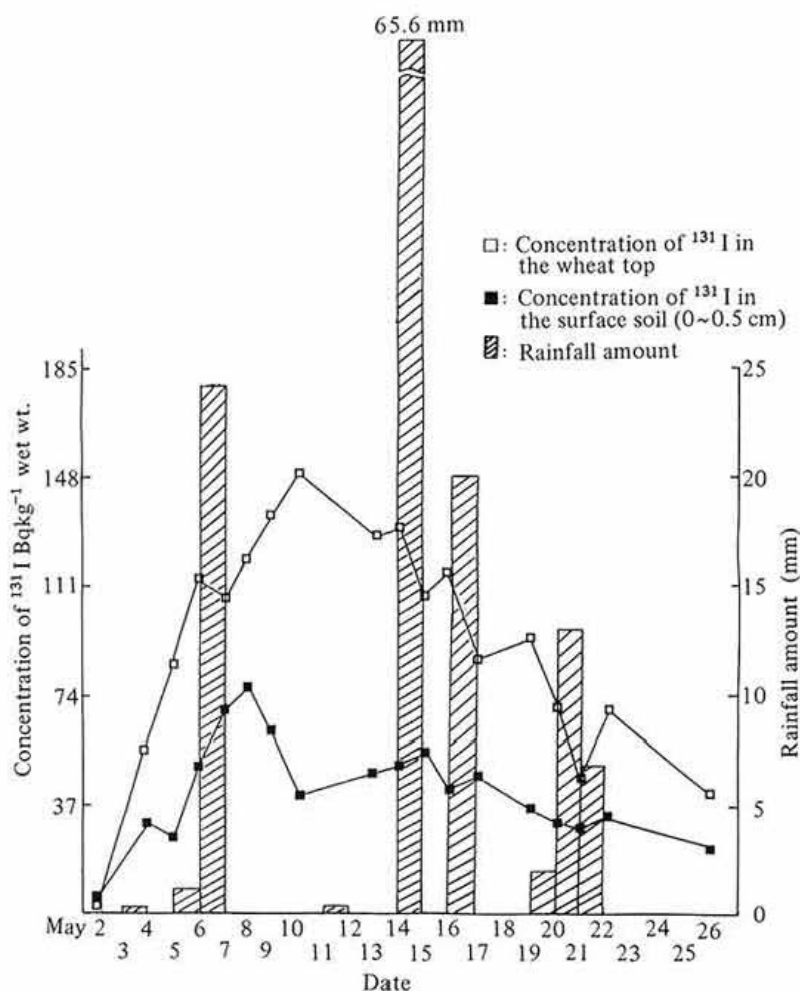
Fig. 2. Changes in the concentration of [131]I[a)] in wheat top and surface
soil (0–0.5 cm), rainfall amount of day[b)41)]
a): Radioactivity at sampling time; AM 9:00–10:00,
b): From the sampling time of the previous day to the same
time on the day.

Dynamics of I and Br in the soil-plant system

1) Abundance and distribution of I and Br in soils and plants

The authors reported on the contents of I and Br in soils and plants of Japan[30–32)]. As shown in Table 2, the average contents of I and Br in soils of the forest lands and upland fields were 43 mg/kg dry wt. and 102 mg/kg dry wt., values which were 10 times larger than the average contents in the world. We could not find any reports from overseas indicating a high level of both elements in soils except for a limited part of soils with salt accumulation or peat bog soils[30)].

The level of Cl in the soils examined was about the same as the average one in the world.

Differences in the contents of I and Br

Table 2. Average contents of the triad elements in soils and plants of Japan[40]

Soil classification	Land utilization	Soil horizon	No. of samples	Content in soil (mg/kg dry wt.)			Plant species	No. of samples	Content in plant leaf (mg/kg dry wt.)		
				I	Br	Cl			I	Br	Cl
Brown Forest soils, Ando soils, etc.	Forest lands	A	103	43	104	117	Arbors and herbs	121	0.49	14	3,540
Ando soils	Upland fields (Tree crops gardens included)	Plow layer	21	43	95	113	Arbors and herbs	23	0.73	53	6,018
Gray Lowland soils, Gley soils, etc.	Paddy fields	Plow layer	31	1.8	5.3	52	Rice plants	30	0.83	20	3,880

among the soil types in forest lands and upland fields of Japan were negligible for the major soil types such as Brown Forest soils and Ando soils. However, the contents of I and Br in paddy soil were almost 10 times lower than those in the forest and upland soils, presumably due to the eluviation of large amounts of I and Br under flooded conditions, during the irrigation period, as described later. The contents of both elements in the leaves of all plants were slightly higher than the average values in the world, presumably because I and Br in soils occur in forms that cannot be easily absorbed by plants.

However, research on the contents of I and Br in soils and plants in the world is still very limited[36]. In the near future, it will be necessary to analyze the content of I and Br in the soil-plant system everywhere in the world, especially in the developing countries.

The figures of the average contents of triad elements along the soil profile of forest and plant leaves based on a model are shown in Fig. 3. Although the difference in the contents of the triad elements in soil, especially horizons A and B, where the plant roots were most abundantly distributed, was comparatively negligible, there was a considerable difference in the contents of the triad elements in plant leaves, i.e. $Cl \gg Br \gg I$. This difference was partly due to the differences in the absorption power of the triad elements by the plants, but, mainly to the variations in the dissolution ratios of the triad elements in the soil solution, as described later.

During the decomposition process from plant leaves to decomposed organic matter through undecomposed fallen leaves, the Cl content decreased remarkably, whereas the I content increased markedly and the Br content increased slightly. These changes were ascribed to the forms of the triad elements in the plant leaves, and more or less to the ratio of water soluble forms in plant leaves.
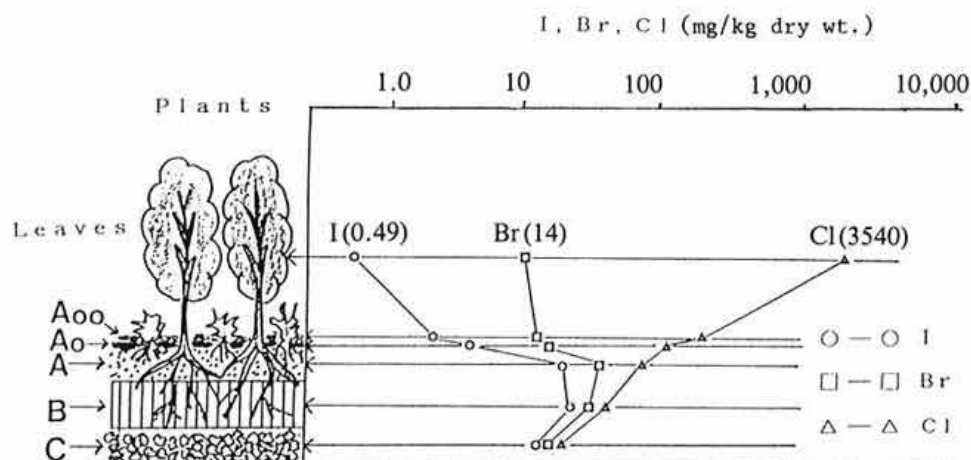
Fig. 3. Contents of the triad elements in the soil-plant system of forest lands in Honshu
island of Japan (average of 34 sites)[40]

2) Dynamics of I and Br in the soil-soil solution system

The authors revealed the following facts in incubation experiments in which the dissolution ratios of the native I and Br in soils changed remarkably according to the environmental conditions of soil (moisture content, pH, temperature, etc.)[42]. The relationship between the soil moisture content and dissolution ratio of the triad elements is shown in Fig. 4. The experiments were carried out as follows: bi-distilled water was added to the air-dried soils to reach a set value of water saturation degree, soils were incubated for 3 weeks at 30°C and the soil solution was collected from the incubated soil by the centrifugation method.

The dissolution ratios of I and Br were lowest under upland field conditions ranging from 40–60% of water saturation. The dissolution ratios of I and Br increased markedly under air-dried conditions (water saturation degree is below 20%) and particularly under flooded conditions. Under flooded conditions, the dissolution ratio of I was several thousand times larger than under upland field conditions.

Dissolution ratio of Cl which did not change

with the variations in the moisture content, was always higher than that of I and Br, and remained relatively constant. The dissolution ratios of the triad elements were in the order of $I \ll Br \ll Cl$ under non-flooded conditions, and such large differences were reflected on the absorbed amounts of the triad elements by plants. Under flooded conditions, since the dissolution ratios of I and Br became very high, differences in the dissolution ratios among the triad elements became less pronounced.

The dissolution ratios of I and Br also changed depending on the differences in pH and temperature of soil under non-flooded conditions.

In the soil reactions, the dissolution ratios of both elements were the lowest in the pH range of 4.0–5.5. The effect of the soil temperature on the dissolution ratios was less pronounced than that of the soil moisture and pH under non-flooded conditions. The dissolution ratios of both elements were lowest in the soil temperature range of 5–30°C.

The soils in the forest lands and upland fields of Japan generally display a water saturation degree of 30–80% (wet conditions) throughout the year and seldom display excessively dry
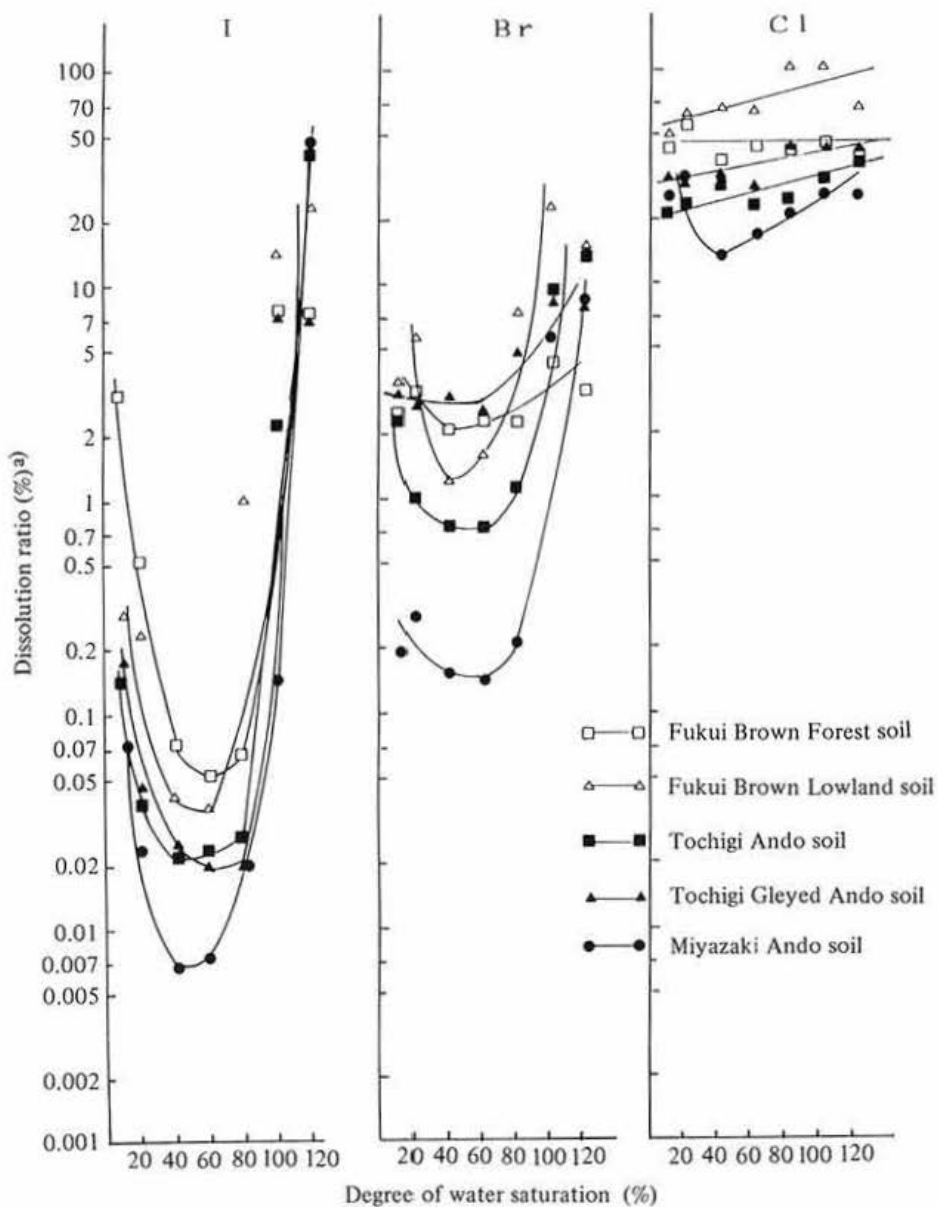
Fig. 4. Relationship between soil moisture content (degree of water saturation) and dissolution ratio of the triad elements[42]

a): Dissolution ratio (%)

$$= \frac{\text{Exuded triad elements in soil solution (mg/kg dry wt.)}}{\text{Total triad elements in soil (mg/kg dry wt.)}} \times 100$$

conditions. Soil reaction is acidic or neutral, and soil temperatures are usually in the range of 0-30°C. These environmental conditions of Japan result in a considerable decrease of the dissolution ratios of I and Br and absorption amount of both elements through the plant roots. On the other hand, such environmental conditions are highly conducive to the deposition and sorption of I and Br falling onto the soil surface from the atmosphere[40].

The low contents of I and Br in paddy soil may be ascribed to the drastic increase in the dissolution ratios of both elements in soil due to flooding of the soil, followed by the runoff of both elements from the soil by percolation of the irrigation water.

3) Existing forms of I and Br in the soil-soil solution system

The author identified quantitatively the individual chemical forms of I in the soil solution obtained under flooded and non-flooded conditions[43]. As shown in Fig. 5, under the non-flooded oxidizing soil conditions, IO_3^- (oxidation no. 5) accounted for 89.0% and I^- (oxidation no. -1) for 6.5%. These results were similar to those obtained for the chemical forms

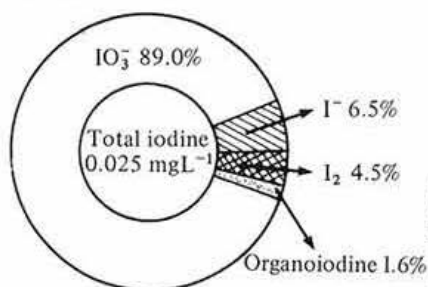of ^{131}I and stable I in rain water collected immediately after the Chernobyl nuclear reactor accident[41].

Furthermore, under non-flooded conditions, the concentration of I in the soil solution was very low, and most of the iodine occurred in an insoluble form in the solid phase of soil. Under the flooded reducing soil conditions, I^- accounted for 90.3% of I in the soil solution, while IO_3^- for only 9.7%. Based on these results, it was assumed that the redox potential controlled the concentration of soluble I or chemical forms of I such as I^- or IO_3^- in the soil solution.

It was reported that I in the soil solid phase was absorbed by anion exchange of I^- or IO_3^- onto the surface of the free oxides of iron and aluminium, and humus[19,21] and an organic iodine compound was formed by the reaction of molecular iodine (I_2) and soil organic matter[17]. The author considers that it is difficult to explain the marked increase of the dissolution ratio of I under flooded reducing soil conditions, without taking account of additional chemical forms or existing forms of I.

The existing forms of Br in the soil solution have not been reported yet. Br in the solid

Non-flooded condition (Upland field condition)   Flooded condition

IO_3^- 89.0%
Total iodine 0.025 mgL^{-1}
I^- 6.5%
I_2 4.5%
Organoiodine 1.6%

I^- 90.3%
IO_3^- 9.7%
Total iodine 1.4 mgL^{-1}
I_2 0.07%
Organoiodine 0%

Method: Soil (Ando soil) was incubated under flooded and non-flooded conditions for 3 weeks at 30°C.
After incubation, soil solution was obtained by centrifugation.
Collected soil solution was immediately fractionated by the solvent extraction method.
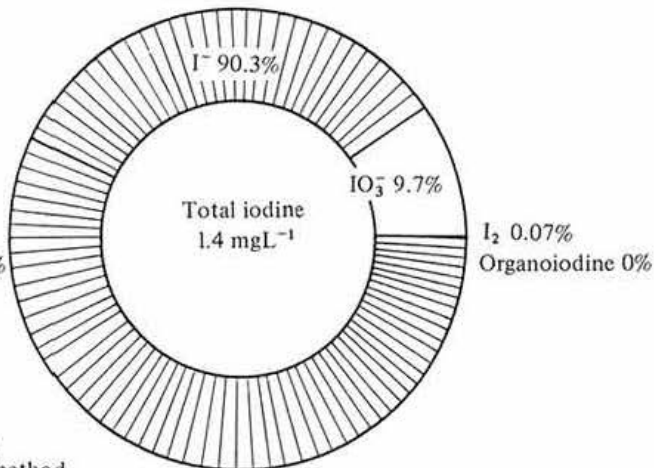
Fig. 5. Chemical forms of iodine in soil solution[43]

phase of soil occurs as an insoluble organic Br compound in humus[20], especially in humic acid, and there was a significantly positive correlation between the carbon content and Br content in the Ando soils with a high content of humus. On the other hand, the authors demonstrated that soil containing a low level of humus and B horizon soil also accumulated a fairly large amount of Br[30–32]. Therefore, it is assumed that Br may occur in another form.

The existing forms of I and Br in the gaseous phase of soil are unknown, including their concentration.

These studies are considered to be important themes for clarifying the dynamics of I and Br in the soil system and soil-atmosphere system.

4) Contents and forms of I and Br in plants

The average content of I in plants (leaves and stems) in the world ranges from 0.2 to 1.0 mg/kg dry wt. and no I accumulator plants with an especially high content can be detected[40]. Even lichens which exhibit the largest amount of I contain only about 10 mg/kg dry wt. and this value is much lower than those of 400–6,000 mg/kg dry wt. recorded in the marine brown algae and red algae[40].

On the other hand, there are considerable differences in the I content (mg/kg dry wt.) among the organs of plants. The average content of I in plants of Japan is shown in Table 3: leaves, 0.46 > fruits, 0.14 > edible roots, 0.055 > seeds, 0.0039. The presence of these large differences among the organs of plants suggests that active intake of green vegetables in addition to algae may enable to prevent goiter.

The existing forms of I in higher plants have not been fully identified. Compounds related to thyroxine were found in some species of halophytes and mesophytes[14]. It was reported that in barley seeds almost all the I is present in the protein fraction[14].

The content of Br in terrestrial plants (leaves and stems) is in the range of 1–30 mg/kg dry

Table 3. Content of I in plant organs[33]

Organs	No. of samples	I content (mg/kg dry wt.)	
		Average	Min.–Max.
Leaves	177	0.46	0.029–2.2
Fruits	32	0.14	0.006–1.7
Edible roots	7	0.055	0.020–0.18
Seeds	10	0.0039	0.00094–0.010

wt. in many wild plants[22]. However, in certain halophytes, the Br content is very close to 740 mg/kg dry wt. which is found in algae living in sea water.

On the other hand, generally, cultivated plants contain a larger amount of Br than wild plants. This phenomenon is caused by the use of pesticides and fertilizers containing Br.

Differences among the organs of plants showed a similar tendency to that of I in that some of them showed a lower content in seeds than in other organs, etc.[23,33]. However, the differences in the Br content among the organs were less pronounced than those of I, and it was difficult to determine the content of Br among the organs, due to possible interference with the fertilizers or chemicals that had been applied.

As regards the existing forms of Br in higher plants, values of 0.1–1.0 mg/kg of organic Br were reported[22]. However data on the chemical forms of organic compounds are not available in the literature. Phacophyceae (brown algae) and Rhodophyceae (red algae) contained organic compounds of CBr_4, CH_2Br_2, etc. with low molecular weight and in some species of algae, Br in the cell liquid was forced out and ran off easily, whereas Br in solid residues such as cell walls, etc., could not be dissolved by washing[22,40].