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LEACHABILITY OF IODINE FROM SOILS OF DIFFERENT LAND USES AS AFFECTED BY SELECTED AMENDMENTS

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Abstract

Iodine is an essential microelement required by humans and animals. Leaching of soils under intensive rains has threatened the fertility status of iodine in soils. Therefore, four discrete amendments were used for the mitigation of iodine leaching from soils. For this study, soils collected from four land uses were mixed with the amendments (gypsum, lime, fly ash, charcoal and sawdust) at the rate of 0, 2.5% and 5% (w/w) in PVC columns. Potassium iodide (KI) was applied to the soil at rate of 100 mg kg⁻¹ and 200mg kg⁻¹. Iodine was determined in water after three leaching events. Results indicated that soil of each land use had apparently influenced the leachability of iodine. Lower amount of iodine was released from the barren and pasture soils as compared to the soils of agriculture and forest land uses. Application of amendments significantly reduced the leaching of iodine from soil. Application of KI increased iodine concentration in the leachate. Across all soils, reduction of iodine leaching or retention of iodine among soil amendments varied in the order charcoal > sawdust > fly ash > gypsum > lime. Overall charcoal and sawdust efficiently reduced iodine leaching than other three amendments. The pH values of the leachate were oppositely associated with the iodine retention of soil. Iodine concentrations in soils were related to the amount of soil organic matter. This study has shown that the retention of iodine in soils could potentially be ameliorated by a suitable soil amendment

Key words: iodine, land uses, leaching, unstructured soils, soil amendments, arid region

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1. Introduction

Iodine is an essential micronutrient. Its deficiency is an important health problem throughout the world. People who live in deficient iodine environment over a long period are prone to iodine deficiency disease (IDD) (Delange, 2005; Preda et al., 2013). Iodine content in the soil varies with region and the soil surface exposed for longer period is subjected to iodine losses via erosion especially in the mountainous areas (Zimmermann, 2012). Generally, iodine is a less abundant element in the environment and soils contain an average of 3 mg kg⁻¹ of total iodine (Johanson, 2003). Iodine is widely but

unevenly distributed in the earth's environment. It has been reported that iodine fate and mobility in soils is dependent on the chemical forms and soil properties, e.g., soil pH, oxidation and reduction processes (Hu et al., 2009; Muramatsu and Wedepohl, 1998). The input of iodine to soil occurs predominantly through transfer from the atmosphere and to a certain extent from dead parts of plants and animals. Weathering of soil parent material make significant contribution. From the atmosphere, iodine is transferred to soils by wet and dry deposition. However, the amount reaching soils through dry deposition is negligible compared to the amount washed out from the soil by rain (Truesdale and Jones, 1996).

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The mobility of iodine species in soils is dependent upon the pH, soil type and ionic condition (Zhang et al., 2013). In soil, inorganic iodine (iodate and iodide) may be retained below pH 6 on positively charged hydrous iron and aluminum oxides and clay mineral edges (Dai et al., 2004; Um et al., 2004). Therefore, sorption would normally be stronger under acidic conditions. Yoshida et al. (1992) observed inorganic iodine sorption up to pH 8. It was also reported that iodate is adsorbed more strongly than iodide, especially in acidic soils with low organic matter contents (Fukui et al., 1996; Yoshida et al., 1992; Shimamoto et al., 2010). This was attributed to the ability of iodate to bond chemically to Fe oxide surfaces through replacement of hydroxyl groups (Fukui et al., 1996; Um et al., 2004). Accumulation of iodine in soil organic matter has been widely reported and humus may constitute the primary reservoir of iodine in most soils (Dai et al., 2009; Steinberg et al., 2008). Due to the iodine biogeochemical transformations in soil (Amachi et al., 2003; Shinonaga et al., 2001), the iodine loss via (bio)volatilization can limit its availability to plants (Muramatsu et al., 2004). The bioavailability of iodine and its translocation depends mainly on iodine interactions with other soil components (Yoshida et al., 1992).

To summarize, iodine content of soil reflects the balance between the input occurred and ability of soil to retain it against leaching. Weng et al. (2008) reported beneficial effects of iodine supplementation to control IDD and improve the environmental iodine content in iodine deficient areas. The bio-iodine in crops and vegetables can serve as a safer iodine resource for human body and an alternative to the iodized salt. 75%–85% of iodine in human body comes from vegetal food under natural conditions (Hetzl et al., 1980). Anke et al. (1995) reported lower iodine content in the soil in inland regions due to the rain eluviation that resulted deficiency of iodine in food chains.

Crops grown in iodine deficient soils are low in iodine concentration and human beings and animals consuming these crops also become deficient in iodine. As mentioned above, iodine retention is affected by the soil organics, clay content and iron ores. It was hypothesized that the use of different amendments would ameliorate retention of supplemented iodine in the soil.

Iodine losses from soils are mainly caused by surface runoff aggravated with poor land uses, high temperature, mineralization rate and leaching etc. Previous research work on the occurrence, retention and leachability of iodine in soils has been poorly reported. Initially, the purpose of this research was to overcome the problem of the iodine leaching from soils of four land uses with varied properties. A study was, therefore, designed to retain the iodine in soils of different land uses instead of being leached down by the application of organic and inorganic amendments.

2. Material and methods

2.1. Soil sampling and analyses

Soil samples (0–20 cm) were collected from surface of four land use systems namely agriculture, barren, pasture and forest situated in the district of Abbottabad, Pakistan. The area is located between 34°92'N latitude and 73°13'E longitude with an altitudinal height of 1260 m. Lithology of the rock formation of Abbottabad area comprises dolomitic limestone. The upper rock formation is enriched with sandstone and lower contact is with shale. A composite soil sample was collected from each land use using an area of 400 m² (20 x 20 m²) and mixed thoroughly in a plastic bag. Soil samples were collected from eight places from Abbottabad area.

Soil samples were air-dried, sieved using a 2-mm sieve. Soils were characterized for major physico-chemical properties as detailed below (Table 1). Moisture contents of the samples were determined by gravimetric method. For this purpose, samples were dried in an oven at 105 °C for 24 hr. Soil bulk density was measured by sampling a predetermined volume of soil using a metal ring inserted into the soil core, and then determined the soil weight (McKenzie *et al.*, 2004). The water holding capacity (%) was measured. Soil texture was determined following Gee and Bauder (1986). The pH of soil (1:5) was determined by a pH meter (HANNA HI 8520). The pH meter was calibrated before measurement with standard buffers at room temperature. Electrical conductivity (EC) of the same 1:5 soil suspension was measured using an EC meter (Model: 4320 JENWAY). Exchangeable cations (Ca, Mg and K) were extracted from soil with ammonium acetate (NH₄OAc) (pH7) solution and the contents were determined using an atomic absorption spectrophotometer (AAS) (Model: AAnalyst 700, Perkin Elmer). Total C was determined by dry combustion (Nelson and Sommers, 1982). The soil samples were weighed up to 100 g in to porcelain crucibles and burned simultaneously in the muffle furnace at 550°C temperature for 2 h. On removal from the oven, samples were placed in glass desiccators and allowed to cool for 30 min. before the initial oven-dry weight was recorded. Total C was calculated based on the weight loss-on-ignition.

2.2. Iodine leaching

A set of polyvinyl chloride (PVC) columns (size: height 40 cm and diameter 15 cm) were mounted vertically on a pre-made wooden frame. A hole was drilled at the bottom of each column for leachate collection. A piece of filter screen was set at the bottom of each column and then washed sand was packed in the column (depth: 5 cm). Unstructured soil (5 kg) was packed into each column. Five discrete amendments (gypsum, slaked lime, fly ash, charcoal and sawdust) were mixed in the surface soil (0-20 cm)

before packing at the rate of 2.5% and 5% (w/w). An unamended soil was used as a control treatment. Gypsum, lime and charcoal were obtained from the local market. Fly ash is the coal combustion product obtained from a thermal power plant. Sawdust were prepared from a local pine tree. Iodine was applied in the form of potassium iodide (KI) at the rate of 100 mg kg⁻¹ and 200 mg kg⁻¹ in solution form. Iodine application rate to soil was based on a previous report (Hong et al., 2008). Three leaching events were conducted using distilled water at a leaching fraction of 0.3-0.4. Leaching fraction was calculated by dividing the volume of drained water by the volume of applied water. Before leaching, distilled water was applied to the soils in the columns at field capacity and then covered to avoid evaporation and incubated for 2 days at room temperature. Leaching was continued until the column was completely drained out. The bottles were placed for leachate on the floor with drainage pipe. Columns were randomized after every 2 days to avoid environmental effects. The columns were covered during the leaching process. Leachate samples were collected from leaching column and were filtered, centrifuged and stored for further analysis. Data regarding total leachate collected and initial water head were recorded. After the leaching events, the soil samples from the PVC column were collected. Selected soil parameters such pH and iodine concentration were determined in dried soil samples collected from each column.

2.3. Iodine determination

Iodine concentrations in both leachate ($\mu\text{g L}^{-1}$) and soil ($\mu\text{g kg}^{-1}$) were determined by the method described by Kaseri et al. (1998). For determination of total amount of iodine in leachate samples, leachate (10 mL) was simply taken and filtered using filter paper Whatman grade 42. For soil, dried soil (0.5 g) was mixed with water (15 mL) and shaken thoroughly for 30 min and filtered. Subsequently, soil and leachate filtrates were centrifuged for 10 min and supernatant was taken and 5% EDTA solution (1 mL) was added. Extractable iodine was determined colorimetrically using a UV spectrophotometer (Model: LI-UV-7000) at 591 nm.

2.4. Statistical analysis

The experiment was a factorial (4 x 5 x 3 x 2) (4 soil types, 5 soil amendments, 3 application rate, 2 KI treatments) resulting in 120 experimental units, arranged into a completely randomized design replicated three times. An average value of iodine concentration for each treatment was calculated. Since iodine concentrations were detected in leached water and soil samples, in minute amount therefore, the units of iodine for the leachate and soil were converted to $\mu\text{g L}^{-1}$ and $\mu\text{g kg}^{-1}$, respectively. Data were statistically analyzed using Statview software (SAS Institute Inc., 1999) and means were separated using least significant difference (LSD) test at 5% level of

probability. Regression plot for iodine concentrations in soils versus C, organic matter and moisture of soils was also calculated using 64 soil samples ($n = 64$).

3. Results and discussion

Soil properties of different land uses: forestry, pasture, agriculture and barren were determined. Land use systems showed different properties of soils and varied to a great extent with clay content, total carbon and cations as shown in Table 1. The moisture level was found significantly higher in the forest soil, while pasture and agricultural soils showed a similar level of moisture at $P \leq 0.05$. Carbon contents in the soils varied as forest > pasture > agriculture > barren land. Concentrations of cationic elements differed as: K > Ca > Mg > Na. The nutrients concentrations were higher in forest soil and lowest in the soils of agricultural and barren land. This phenomenon could be associated with the constant litter falls and the process of nutrient transformations under vegetation cover. Chen et al. (2003) reported enhanced nutrient cycling due to vegetation, which also influenced soil properties and plant nutrient availability. Forest species recycle plant nutrient depending on the litter fall and litter chemical composition (Mlambo et al., 2005). These soils differed significantly in iodine concentration, as it was 0.35 mg kg⁻¹ in agricultural soil, 0.04 mg kg⁻¹ in barren soil, 0.66 mg kg⁻¹ in forest soil and 0.54 mg kg⁻¹ in pasture soil. Regression analysis showed iodine concentrations in soils satisfactorily related to the amount of soil moisture ($R^2 = 0.68$) and soil carbon or organic matter of soils ($R^2 = 0.77$) (Fig. 1).

Primarily the purpose of this study was to investigate the influence of selected amendments on the leachability of iodine from soils of four land uses (Figs. 2-5). The study indicated that land use had close relationship with the soil quality and iodine concentrations. Iodine leaching from soils was decreased with the application of amendment material. All amendments apparently reduced iodine loss via leaching as compared to the un-amended soil at $P \leq 0.05$ irrespective of the soil. The soil exhibited different retention capacity for iodine after amendments. The addition of amendment significantly reduced iodine leaching from soil especially at higher rate of application. Loss of iodine from the soil column was higher with elevated KI dose. The soil amendments differed for iodine retention in soil column as charcoal > sawdust > fly ash > gypsum > lime.

There were marked differences in iodine content among land use patterns. Across all amendments, iodine leaching from soil column varied according to the land uses. It was found that, among the four types of soils, the higher retention of iodine was in the soils of forest and agricultural land uses as compared to the soils of pasture and barren land uses at KI application of 200 mg kg⁻¹. This revealed that iodine contents of soils have been fluctuated by iodine supply and retention ability iodine by soil.

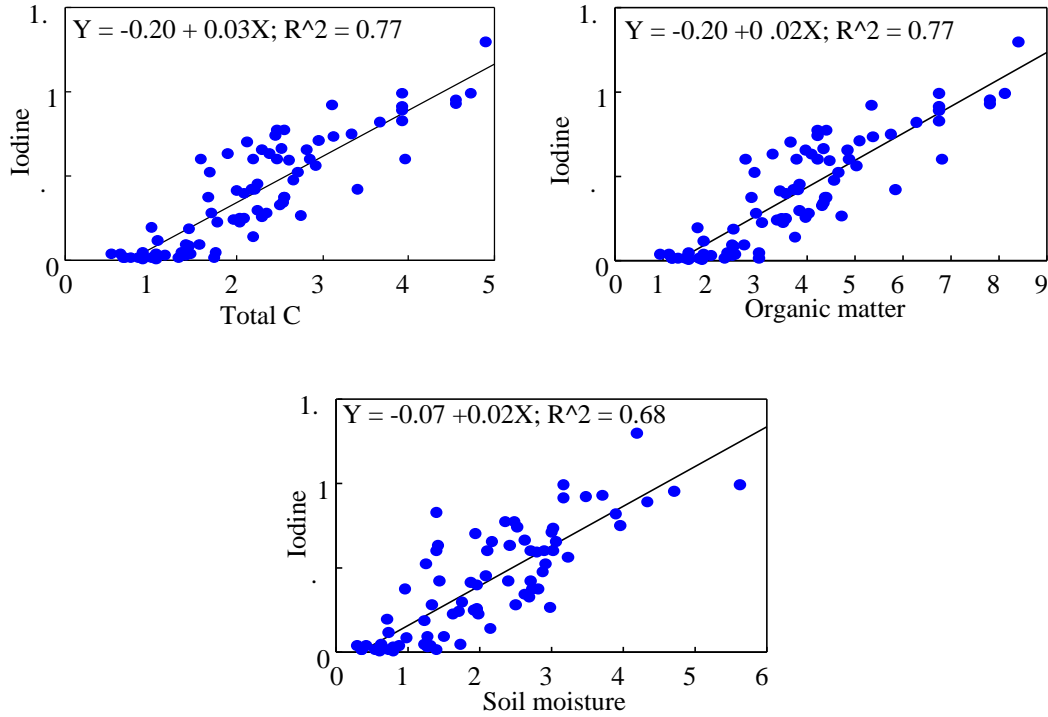


Fig. 1. Regression plot for total iodine concentration vs. C, organic matter and soil moisture of soil (n = 64) : (a) represents iodine contents of soil vs. total C, (b) represents iodine contents of soil vs. organic matter, (c) represents iodine contents of soil vs. soil moisture

Table 1. Properties of soils collected from four land uses (agriculture, barren, forest and pasture)*

Parameter	Forest	Agriculture	Barren	Pasture	LSD (0.05)
Sand (%)	68.7±3.8	75.6±6.9	81.1±4.6	69.2±3.6	4.3
Silt (%)	17.0±1.4	16.6±1.2	12.5±1.0	9.2±0.6	3.8
Clay (%)	14.3±1.0	7.8±0.6	6.4±0.6	21.6±1.3	5.4
Texture	Sandy loam	Sandy loam	Loamy sand	Sandy loam	
Total C (g kg ⁻¹)	50.2±3.2	21.6±1.3	32.5±2.3	15.6±1.0	5.6
Moisture (%)	26.3±1.6	18.2±1.0	12.2±1.0	21.2±1.2	2.3
Bulk density (g cm ⁻³)	1.45±0.02	1.52±0.03	1.62±0.02	1.56±0.02	0.08
Total iodine (µg g ⁻¹)	0.66±0.2	0.34±0.02	0.12±0.01	0.54±0.1	0.02
Exch. Ca (mg kg ⁻¹)	186.6±8.9	76.3±6.8	125.3±5.6	149.3±2.0	9.9
Exch. Mg (mg kg ⁻¹)	51.3±3.6	56.7±3.8	43.1±2.9	41.9±2.2	5.9
Exch. K (mg kg ⁻¹)	215.5±9.8	156.0±5.6	189.2±6.7	171.0±7.3	9.6
Exch. Na (mg kg ⁻¹)	23.9±1.3	35.6±2.4	17.6±1.6	26.3±1.8	3.6
CEC (mg kg ⁻¹)	476±12.6	324±9.2	375±10.4	388±12.9	10.3
EC (1:5) (µS m ⁻¹)	156±10.2	125±9.6	88±6.8	92±7.6	8.6
pH (1:5)	6.8±0.2	7.6±0.2	7.9±0.2	7.8±0.2	0.3

Notes: *± values indicate the standard errors (n = 8).

Iodine contents in the leachate of a soil could be related to soil properties. Five percent charcoal amendment significantly reduced iodine content in the leachate by 53% in forest soil, 42% in barren soil, 54% in agriculture and 60% in pasture soil when KI was applied at the rate of 100 mg kg⁻¹ (Table 2). Following lime application, reductions in iodine leaching from soils were significant i.e., 8% for forest soil, 19% for barren soil, 29% for agricultural soil and 31% for pasture soil at KI application of 100 mg kg⁻¹. Iodine leaching was reduced by 21, 26, 28 and 29% in forest, barren, agriculture and pasture soils, respectively after KI application (at 100 mg kg⁻¹) under 5% gypsum

amendment. For the 5% sawdust, it was reduced by 51% in forest, 53% in barren, 56% in agriculture and 55% in pasture soil when added with 100 mg kg⁻¹ of KI.

Iodine concentration found in the leachate of respective soil after amendment with 5% fly ash was 8 µg L⁻¹ in forest, 4 µg L⁻¹ in barren, 7 µg L⁻¹ in agriculture and 7.5 µg L⁻¹ in pasture soil when supplemented with 100 mg iodine kg⁻¹. The unamended soil released iodine in the order of 17 µg L⁻¹ from forest soil, 7.5 µg L⁻¹ from barren soil, 15 µg L⁻¹ from agricultural soil and 14 µg L⁻¹ from pasture soil. The lower iodine concentration in the leachate of

soil (i.e., barren land) may be linked to the combination of lower organic matter inputs.

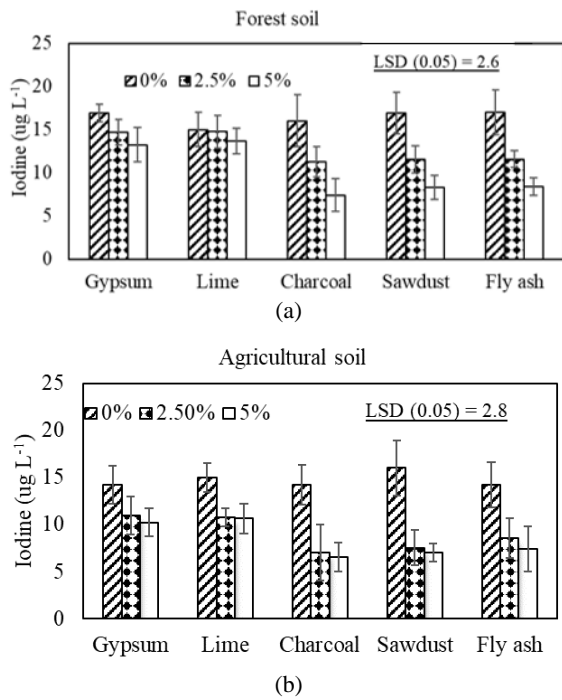


Fig. 2. Leachability of iodine as affected by soil amendment after 100 mg kg⁻¹ of KI application: (a) represents iodine concentration in leachate collected from forest soil, (b) represents iodine concentration in leachate collected from agricultural soil

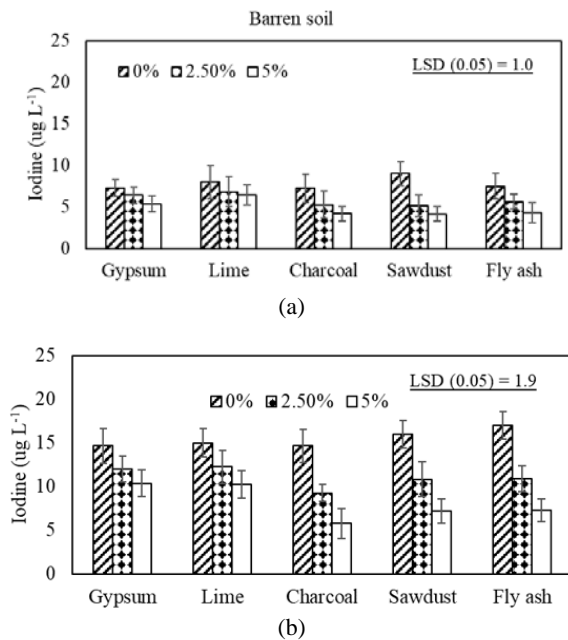


Fig. 3. Leachability of iodine as affected by soil amendment after 100 mg kg⁻¹ of KI application: (a) represents iodine concentration in leachate collected from barren soil, (b) represents iodine concentration in leachate collected from pasture soil

With the higher application rate of KI (200 mg kg⁻¹) in the amended soil, the leaching of iodine also enhanced. Sawdust application significantly reduced

iodine concentration in the leachate by 51% for the forest soil, 53% for barren soil, 56% for agricultural soil and 55% for pasture soil at KI application of 100 mg kg⁻¹.

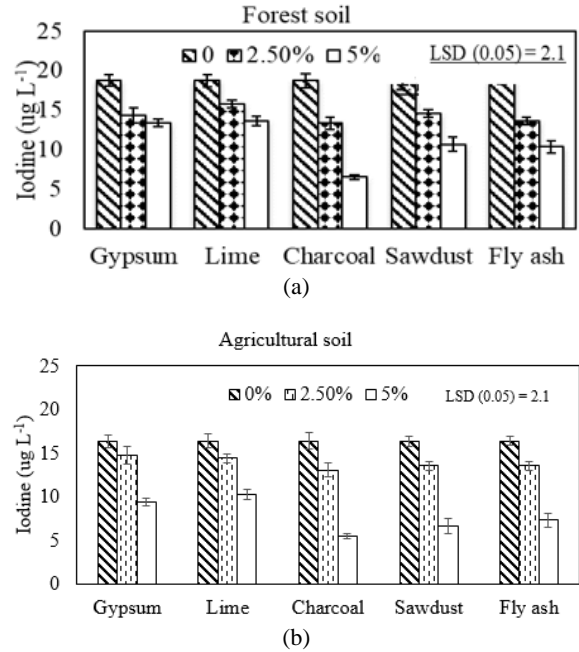


Fig. 4. Leachability of iodine as affected by soil amendment after 200 mg kg⁻¹ of KI application: (a) represents iodine concentration in leachate collected from forest soil, (b) represents iodine concentration in leachate collected from agricultural soil

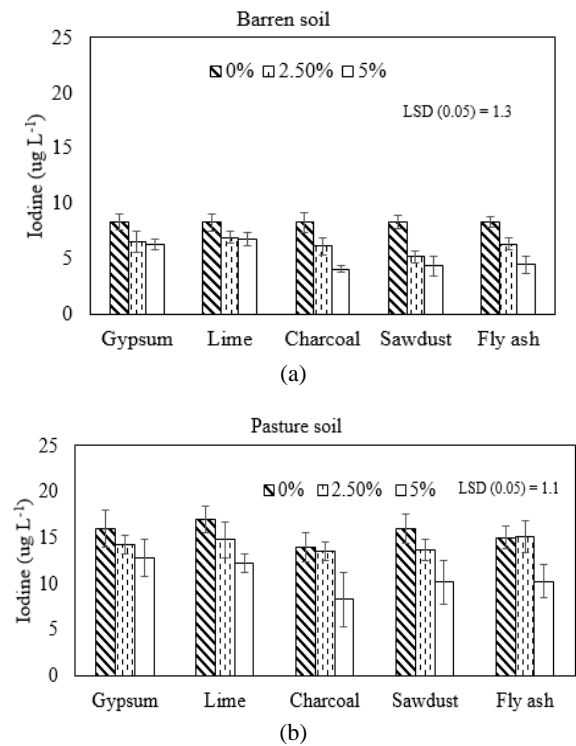


Fig. 5. Leachability of iodine as affected by soil amendment after 200 mg kg⁻¹ of KI application: (a) represents iodine concentration in leachate collected from barren soil, (b) represents iodine concentration in leachate collected from pasture soil

With the higher application rate of KI (200 mg kg⁻¹) in the amended soil, reduction in iodine concentration was obtained after amendment with 5% of charcoal, sawdust, fly ash and gypsum and lime were 65, 43, 44, 28 and 27 % in forest soil, respectively.

At 5% application rate, iodine concentrations in the leachate from agricultural soil was reduced by 66% for charcoal, 59% for sawdust, 55% for fly ash, 42% for gypsum and 37% for lime. Reduction in iodine concentrations obtained after amendment with 5% of charcoal, sawdust, fly ash, gypsum and lime were 42, 53, 42, 26 and 19% in barren soil, respectively, when compared with the control (unamended) soil after KI application at the rate of 200mg kg⁻¹. Iodine in the leachate was significantly reduced in the pasture soil (*P* ≤ 0.05) after 5% application of amendment by 60% in charcoal, 55% sawdust, 57% fly ash, 29% in gypsum and 31% in lime. The maximum iodine was retained at 200 mg kg⁻¹ treatment of 5% charcoal amended soil. The agricultural soil retained 66% of the iodine followed by forest (65%), barren (50%) and pasture soil (48%). This study ascertained that waste material of charcoal, fly ash and sawdust can be viably recycled to reduce iodine losses from soils via leaching. The leachability of iodine was apparently associated with iodine concentration of soil. Mixing of a soil with the selected amendment can alter the extractability of iodine. Iodine was released from each soil column according to the application rate of an amendment as 0 > 2.5% > 5%. This reduction phenomenon of iodine could also be associated with the physico-chemical changes that occurred in soil after the application of the amendment. Generally, coarse-textured soils are low in fertility status and poor in organic matter and water-

holding capacity. This study indicated that the leachability of iodine depended on soil amendments that may in turn associated with the changes in soil physico-chemical properties, i.e., soil porosity, increased moisture capacity. For instance, Abdelhafez et al. (2014) reported a highly porous structure, high surface area, pH, cation exchange capacity (CEC), adsorptive capacity, carbon content, organic matter content, and high water-holding capacity have been reported for biochar. Irshad et al. (2014) reported that leachability of nitrate from sandy soil reduced after application of soil amendments and nitrate retention in the soil varied among materials in the order of manure > charcoal > wood ash > sawdust. The iodine content in the leachate of the soil has been observed depending on the ability of the amendment to retain the supplemented iodine. Hong et al. (2012) reported that the amounts of iodine desorbed from soils differed depending on the type of soil. It has been reported that soil properties like cation exchange capacity, organic matter and clay minerals affected iodine adsorption and bioavailability (Yoshida et al., 1992).

Soil amendments like lime and gypsum significantly raised the pH of soil leachate (Table 3). Soils without amendments showed the pH values in the leachate as agriculture (7.48) > forest (7.47) > pasture (7.45) > barren (7.27). After treatments pH values differed as lime > gypsum > fly ash > sawdust > charcoal irrespective of the soil of any land use. Soil amendments like gypsum and lime significantly raised the pH of soil leachate (Table 2; Figs. 6-7). Leachate from the control column of forest soil had pH values of 7.47 and 7.56 at 100 mg kg⁻¹ and 200 mg kg⁻¹ KI treatments, respectively. After application of 5% charcoal pH values of the leachate decreased to 6.57 and 6.43 in the same KI treated soils.

Table 2. Iodine retention (%) in soil as affected by different amendments after application of potassium iodide (KI) at the rate of 100 mg kg⁻¹ and 200 mg kg⁻¹

Land use	Amendment	100 mg kg ⁻¹ KI		200 mg kg ⁻¹ KI	
		2.5%	5%	2.5%	5%
Forest soil	Gypsum	13.1±1.2	21.7±1.6	23.5±1.6	28.4±2.3
	Lime	11.6±1.3	13.7±0.8	16.0±1.0	27.4±2.0
	Charcoal	29.6±2.5	53.9±2.6	28.8±2.1	65.1±4.2
	Sawdust	31.8±2.4	51.0±2.5	22.0±1.6	43.1±3.2
	Fly ash	31.9±2.6	50.6±2.3	27.4±1.8	44.7±2.9
Agricultural soil	Gypsum	11.8±1.0	26.0±1.6	10.2±0.8	42.6±2.8
	Lime	14.6±1.4	19.0±1.5	12.1±1.2	37.4±2.2
	Charcoal	27.4±2.0	42.3±2.8	20.5±1.6	66.2±3.6
	Sawdust	42.6±3.6	53.7±2.7	17.2±1.0	59.4±3.4
	Fly ash	24.8±1.9	42.8±2.5	17.1±1.7	55.2±3.0
Barren soil	Gypsum	23.0±1.8	28.1±1.9	21.2±1.6	24.3±2.1
	Lime	28.3±2.6	29.0±1.8	16.3±1.5	17.9±1.8
	Charcoal	50.5±3.5	54.0±2.7	26.0±1.8	50.8±3.4
	Sawdust	52.9±2.8	56.1±2.4	37.5±2.2	47.3±3.1
	Fly ash	39.8±2.1	48.1±2.1	23.4±1.8	46.0±2.8
Pasture soil	Gypsum	18.1±1.6	29.2±1.6	11.1±0.9	20.2±1.5
	Lime	18.2±1.6	31.7±1.5	7.8±0.5	23.7±1.4
	Charcoal	36.9±2.1	60.6±3.1	15.1±1.0	48.4±2.4
	Sawdust	32.4±2.7	55.0±3.0	14.6±1.0	36.7±2.0
	Fly ash	36.1±2.3	57.3±3.5	5.7±0.4	35.8±1.9
	LSD (0.05)	3.2	5.6	3.8	5.9

Note: *± values indicate the standard errors (n = 3).

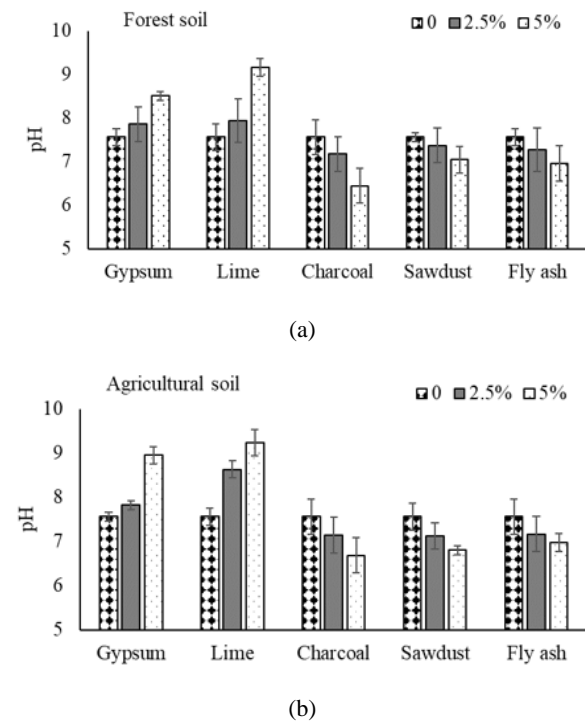
Table 3. pH of leachate from soil as affected by amendment at 100 mg kg⁻¹ KI application

Amendment	Application rate (%)	Forest	Agriculture	Barren	Pasture
Control	0	7.47	7.48	7.27	7.45
Gypsum	2.5	7.55	7.75	7.43	7.63
	5.0	8.63	8.43	8.38	8.24
Lime	2.5	7.87	7.87	7.57	7.98
	5.0	8.73	8.55	8.36	8.64
Charcoal	2.5	7.06	7.13	7.12	7.14
	5.0	6.57	6.89	6.92	6.98
Sawdust	2.5	7.16	7.15	7.14	7.24
	5.0	6.94	6.90	6.97	7.10
Fly ash	2.5	7.19	7.22	7.23	7.30
	5.0	7.04	6.95	7.15	7.14
	LSD (0.05)	0.12	0.16	0.20	0.17

The pH values of leachate of forest soil were 6.94 in 5% sawdust, 7.04 in 5% fly ash, 8.73 in 5% lime and 8.63 in 5% gypsum treatments at 100 mg kg⁻¹ KI. pH values found in the barren soil were 6.92 with 5% charcoal, 6.97 with 5% sawdust, 7.15 with 5% fly ash, 9.38 with 5% lime and 8.38 with 5% gypsum treatments. Agricultural soil achieved the pH values in the 5% treatments as 8.55 (lime) > 8.43 (gypsum) > 6.95 (fly ash) > 6.90 (sawdust) > 6.89 (charcoal) at 100 mg kg⁻¹ KI. Pasture soil gave pH values after 5% application of amendment as 8.64 in lime > 8.24 in gypsum > 7.14 in fly ash > 7.10 in sawdust > 6.98 in charcoal. In soil supplemented with 200 KI, the pH values of the leachate collected from the soil enhanced from 7.47 to 7.55 in forest soil, from 7.27 to 7.58 in barren soil, from 7.48 to 7.55 in agricultural soil, from 7.45 to 7.62 in pasture soil.

Generally, pH, organic content and iron content of the soil affect the iodine retention in soil. In this study the amendment which lowered the pH of leachate retained higher iodine concentration in soil. For instance, charcoal and sawdust reduced the pH and thus enhanced iodine retention in the soil column (Table 3; Fig. 8). In forest soil, 5% charcoal amended soil reduced iodine leaching and enhanced the retention by 65% as compared to the no amendment at 200 mg kg⁻¹ KI treatment. Charcoal treatment (5%) reduced the pH of soil from 7.56 to 6.4 at 200 mg kg⁻¹ KI treatment. Iodine retention (%) enhanced with the higher application of KI in soil columns. For gypsum and lime amended soil both at 100 and 200 mg kg⁻¹ KI treatments, pH of the leachate was increased possibly by releasing the Ca²⁺ ions. Both gypsum and lime amended soil showed lower ability for iodine retention irrespective of the soil. Johansson (2003) reported the highest amount of iodine loss from soils with pH below 5 and organic content below 3%. Pasture soil amended with the charcoal showed higher iodine retention (48%) in soil column. In the same soil sawdust retained 36.7% followed by fly ash which retained 35.8% of I in soil at 5% application. Factors that decrease the sorption of iodine in soils included anoxic redox conditions, increasing salinity and the concentration of competing anions, increasing pH and clay mineral content (Muramatsu and Yoshida, 1999; Yoshida et al., 1998). The mobility of iodine species in soils was reported to be dependent upon the pH,

type and ionic status of soil (Zhang et al., 2013). pH affects the sorption and migration of iodide and iodate in soil greatly as the pH of the solution increases, the sorption of iodine species decreases both in the mineral and organic soils (Sheppard, 2003; Um et al., 2004). Soils with significant quantities of silt, clay, and organic matter retained more NO₃-N (Irshad et al., 2014). Irshad et al. (2014) reported a reduced nitrate leaching from sandy soil after using different waste materials. Bigelow et al. (2001) found that ammonium leaching was directly proportional to the CEC of the amendments. Knowles et al. (2011) reported reduced nitrate leaching from biochar plus biosolid-amended soils than control treatments. Summary of analysis of variation (ANOVA) on the effect of amendments and soils on iodine leaching and pH of leachate (at 200 mg kg⁻¹ KI application) is given in Table 4.

**Fig. 6.** pH of leachate as affected by soil amendments at 200 mg kg⁻¹ KI application: (a) represents pH changes in leachate collected from forest soil, (b) represents pH changes in leachate collected from agricultural soil

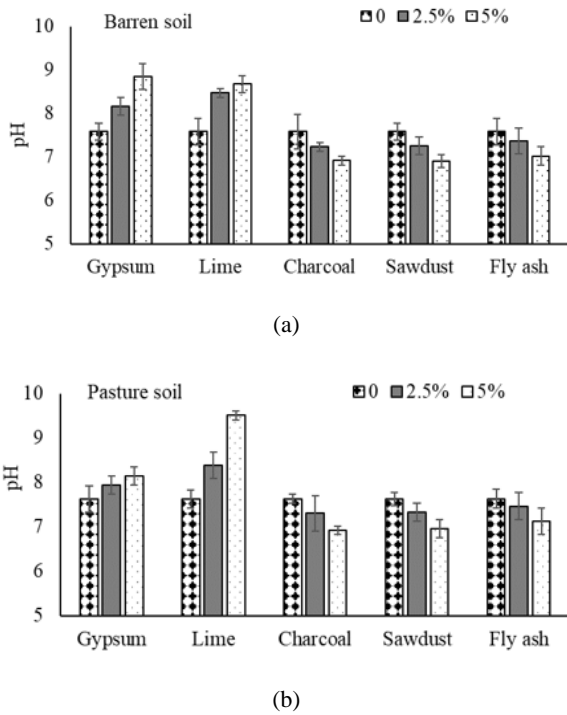


Fig. 7. pH of leachate as affected by soil amendments at 200 mg kg⁻¹ KI application: (a) represents pH changes in leachate collected from barren soil, (b) represents pH changes in leachate collected from pasture soil

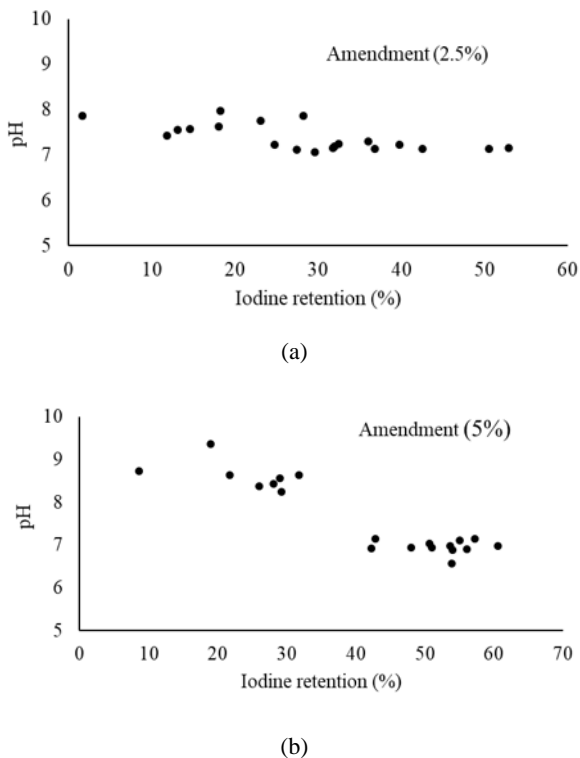


Fig. 8. Relationship of iodine retention (%) in soil column versus pH of leachate after 2.5 and 5% amendment application: (a) represents relationship between pH of leachate and iodine retention in soil at 2.5% amendment application, (b) represents relationship between pH of leachate and iodine retention in soil at 5% amendment application

Table 4. Summary of analysis of variation (ANOVA) on the effect of amendments and soils on iodine leaching and pH of leachate (at 200 mg kg⁻¹ KI application)

Source of variation	Concentration of iodine in leachate	pH of leachate
	F value	
Soil (S)	17.4**	107.0**
Amendment (A)	61.2**	21.2**
S x A	5.67*	NS

Notes: *, ** = Significant at P<0.05 and 0.01, respectively, NS= Not-significant

4. Conclusions

Iodine concentrations in the leachate were relatively higher from the forest and pasture soils as compared to the barren. Iodine contents in soils were associated to the amount of soil organic matter and soil moisture. Leachability of iodine was largely differed by the amendment material and reduced from the soil column.

Regardless to the soil, the retention of iodine across all amendments measured as charcoal > sawdust > fly ash > gypsum > lime. The pH values of the leachate were associated with the retention of iodine of soil. This research signifies the use of amendments for retention of iodine in soils. The surface characterization of amended and unamended soils is a limitation of this study. Therefore, analyzing the micro-morphological properties and chemical composition of soils using scanning electron microscopy coupled with energy dispersive X-ray (SEM / EDX) techniques would be carried out during a separate study.

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References

Abdelhafez A.A., Li J., Abbas M.H.H., (2014), Feasibility of biochar manufactured from organic wastes on the stabilization of heavy metals in a metal smelter contaminated soil, *Chemosphere*, **117**, 66-71.
 Amachi S., Kasahara M., Hanada S., Kamagata Y., Shinoyama H., Fujii T., Muramatsu Y., (2003), Microbial participation in iodine volatilization from soils, *Environmental Science and Technology*, **37**, 3885-3890.
 Anke M., Groppe B., Muller M., Scholz E., Kramer K., (1995), The iodine supply of humans depending on site, food offer and water-supply, *Fresenius' Journal of Analytical Chemistry*, **352**, 97-101.
 Bigelow A.C., Bowman D.C., Cassel D.K., (2001), Nitrogen leaching in sand-based root zones amended with inorganic soil amendments and sphagnum peat, *Journal of the American Society of Horticultural Science*, **126**, 151-156.
 Dai J.L., Zhang M., Hu Q.H., Huang Y.Z., Wang R.Q., Zhu Y.G., (2009), Adsorption and desorption of iodine by various Chinese soils: II. Iodide and iodate, *Geoderma*, **153**, 130-135.

- Dai J.L., Zhang M., Zhu Y.G., (2004), Adsorption and desorption of iodine by various Chinese soils I. iodate, *Environment International*, **30**, 525-530.
- Delange F., (2005), Epidemiology and impact of iodine deficiency in pediatrics, *Journal of Pediatric Endocrinology and Metabolism*, **18**, 1245-1251.
- Fukui M., Fujikawa Y., Satta N., (1996), Factors affecting interaction of radioiodide and iodate species with soil, *Journal of Environmental Radioactivity*, **31**, 199-216.
- Gee G.W., Bauder J.W., (1986), *Particle-Size Analysis*, In: *Methods of Soil Analysis, Part 1. Physical and Mineralogical Methods*, Agronomy Monograph No. 9, 2nd Edition, American Society of Agronomy/Soil Science Society of America, Klute A. (Ed.), Madison, WI, 383-411.
- Hetzel B.S., Thilly C., Fierro-Benitez R., Petrell E.A., Butterfield J.H., Stanbury J.B., (1980), *Iodized Oil in the Prevention of Endemic Goiter and Cretinism*, In: *Endemic Goiter and Cretinism-Iodine Nutrition in Health and Disease*, Stanbury J.B., Hetzel B.S. (Eds.), John Wiley, New York, 513-532.
- Hong C., Weng H., Jilani G., Yan A., Liu H., Xue Z., (2012), Evaluation of iodide and iodate for adsorption-desorption characteristics and bioavailability in three types of soil, *Biological Trace Element Research*, **146**, 262-271.
- Hong C.L., Weng H.X., Qin Y. C., Yan A.L., Xie L.L., (2008), Transfer of iodine from soil to vegetables by applying exogenous iodine, *Agronomy for Sustainable Development*, **28**, 575-583.
- Hu Q., Moran J. E., Blackwood V., (2009), *Geochemical Cycling of Iodine Species in Soils*, In: *Comprehensive Handbook of Iodine Nutritional, Biochemical, Pathological and Therapeutic Aspects*, Preedy V.R., Burrow G.N., Watson R., (Eds.), London: Academic Press, 93-105.
- Irshad M., Waseem A., Umar M., Sabir M.A., (2014), Leachability of nitrate from sandy soil using waste amendment, *Communications in Soil Science and Plant Analysis*, **45**, 680-687.
- Johanson K.J., (2003), *Iodine in Soil- A Technical Report*, TR-00-21 Svensk Kärnbränslehantering AB, Stockholm Sweden. <http://193.235.25.3/upload/publications/pdf/TR-00-21webb.pdf>.
- Knowles O.A., Robinson B.H., Contangelo A., Clucas L., (2011), Biochar for the mitigation of nitrate leaching from soil amended with biosolids, *Science of the Total Environment*, **409**, 3206-3210.
- McKenzie N., Jacquier D., Isbell R., Brown K., (2004), *Australian Soils and Landscapes: An Illustrated Compendium*, CSIRO Publishing, Collingwood, Victoria.
- Mlambo D., Nyathi P., Mapaure I., (2005), Influence of *Colophospermum mopane* on surface soil properties and under-storey vegetation in a southern African savanna, *Forest Ecology and Management*, **212**, 394-404.
- Muramatsu Y., Wedepohl H.K., (1998), The distribution of iodine in the earth's crust, *Chemical Geology*, **147**, 201-216.
- Muramatsu Y., Yoshida S., (1999), Effects of microorganisms on the fate of iodine in the soil environment, *Geomicrobiology Journal*, **16**, 85-93.
- Muramatsu Y., Yoshida S., Fehn U., Amachi S., Ohmomo Y., (2004), Studies with natural and anthropogenic iodine isotopes: iodine distribution and cycling in the global environment, *Journal of Environmental Radioactivity*, **74**, 221-232.
- Nelson D.W., Sommers L.E., (1982), *Total Carbon, Organic Carbon and Organic Matter*, In: *Methods of Soil Analysis. Part 2. Chemical and Microbiological Properties*, Page A.L., Miller R.H., Keeney D.R., (Eds.), ASA, SSSA, Madison, WI, USA, 539-580.
- Preda C., Ungureanu M.C., Leustean L., Cristea C., Mogos V., Vulpoi C., Gavrilescu M., (2013), Human health related to iodine environmental occurrence and its deficiency in water and food, *Environmental Engineering and Management Journal*, **12**, 1045-1049.
- SAS Institute Inc. (1999), *Base SAS® 9.3 Procedures Guide*. Cary, NC: SAS Institute Inc. Cary, NY, USA.
- Sheppard S.C., (2003), Interpolation of solid/liquid partition coefficients, K_d, for iodine in soils, *Journal of Environmental Radioactivity*, **70**, 21-27.
- Shimamoto Y.S., Itai T., Takahashi Y., (2010), Soil column experiments for iodate and iodide using K-edge XANES and HPLCICP- MS, *Journal of Geochemical Exploration*, **107**, 117-123.
- Shinonaga T., Gerzabek M.H., Strelb F., Muramatsu Y., (2001), Transfer of iodine from soil to cereal grains in agricultural areas of Austria, *Science of the Total Environment*, **267**, 33-40.
- Steinberg S.M., Buck B., Morton J., Dorman J., (2008), The speciation of iodine in the salt impacted Black Butte soil series along the Virgin river, Nevada, USA, *Applied Geochemistry*, **23**, 3589-3596.
- Truesdale V.W., Jones S.D., (1996), The variation of iodate and total iodine in some UK rainwaters during 1980-198, *Journal of Hydrology*, **179**, 67-86.
- Um W., Serne R.J., Krupka K.M., (2004), Linearity and reversibility of iodide adsorption on sediments from Hanford, Washington under water saturated conditions, *Water Research*, **38**, 2009-2016.
- Weng H.X., Weng J.K., Yan A.L., Hong C.L., Yong W.B., Qin Y.C., (2008), Increment of iodine content in vegetable plants by applying iodized fertilizer and the residual characteristics of iodine in soil, *Biological Trace Element Research*, **123**, 218-228.
- Yoshida S., Muramatsu Y., Uchida S., (1992), Studies on the sorption of I⁻ (Iodide) and IO₃⁻ (Iodate) onto Andosols, *Water, Air, and Soil Pollution*, **63**, 321-329.
- Yoshida S., Muramatsu Y., Uchida S., (1998), Soil-solution distribution coefficients, K_ds, for I⁻ and IO₃⁻ for 68 Japanese soils, *Radiochimica Acta*, **82**, 293-297.
- Zhang S., Xu C., Creeley D., Ho Y.F., Li H.P., Grandbois R., Santschi P.H., (2013), Iodine-129 and Iodine-127 speciation in groundwater at the Hanford site, US: iodate incorporation into calcite, *Environmental Science and Technology*, **47**, 9635-9642.
- Zimmermann M.B., (2012), *Iodine and Iodine Deficiency Disorders*, In: *Present Knowledge in Nutrition*, 10th Edition, Erdman J.W.J., Macdonald I.A., Zeisel S.H., (Eds.), John Wiley & Sons, Oxford, UK, 554-567.