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Sorption and speciation of iodine in boreal forest soil

Mervi Söderlund[1] · Juhani Virkanen[2] · Hanna Aromaa[1] · Nadezda Gracheva[3,4] · Jukka Lehto[1]

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Abstract The speciation and sorption of iodine was studied on humus and mineral soil samples in the initial chemical forms of iodide and iodate. Iodate was reduced to iodide in significant amounts especially in anaerobic soil conditions and in low pH. An unidentified, possible organo–iodine species was detected in humus samples and in aerobic mineral soil at incubation times of 1–21 days and in low pH (4–5). The overall retention of iodide and iodate on Olkiluoto mineral soil was very weak and organic matter proved to be the main sorbent for iodine.

Keywords Iodide and iodate · Olkiluoto soil · Speciation · Sorption · HPLC–ICP-MS

Introduction

The Finnish concept for the final disposal of spent nuclear fuel from the current nuclear power plants is based on the concealment of the spent fuel without reprocessing in an underground repository. Olkiluoto Island, a large island situating on the coast of the Baltic Sea in southwestern Finland, was selected as the final disposal site and currently the repository is being built in its granitic bedrock at depths of 400–450 m [1]. The target of the final disposal concept is the isolation of the fuel from its environment by the host bedrock and engineered barriers, i.e. copper canisters with cast-iron inserts and bentonite buffer surrounding the canisters. The integrity of the copper canisters is expected to last at least for the first 100,000 years, during which the short–lived and intermediate–lived radionuclides would have safely decayed [2, 3]. However, in circumstances where a copper canister malfunctions, radionuclides could possibly escape from the repository into the near-field geosphere and migrate into far-field environments, the overburden and biosphere—a scenario which is of great importance in the safety assessment of spent nuclear fuel especially in the context of long-lived radionuclides [2].

^{129}I is considered as one of the highly important radionuclides according to its possible future dose for man [4] based on its long physical half-life of 15.7×10^6 years, and its presence as an anionic species. It is expected to have a low level interaction with solid phases thereby leading to a potentially high migration rate. ^{129}I is produced in the fission of ^{235}U and ^{239}Pu with a fission yield of 0.71 and 1.41 %, respectively. In addition to human nuclear practices, ^{129}I is a naturally occurring radionuclide produced in small quantities from xenon in the upper atmosphere by cosmic–ray interactions [5]. In all, iodine is a widely-spread element within the atmosphere, lithosphere and biosphere and forms a wide variety of compounds with diverse properties [6–8]. The average content of iodine in European topsoil is 3.94 mg kg^{-1} [9].

In soil systems the speciation and behaviour of iodine is primarily governed by the ambient redox potential and microbial activity [6, 8, 10–12]. In well–oxidised

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✉ Mervi Söderlund
mervi.soderlund@helsinki.fi

[1] Laboratory of Radiochemistry, Department of Chemistry, University of Helsinki, P.O. Box 55, 00014 Helsinki, Finland

[2] Department of Geosciences and Geography, University of Helsinki, P.O. Box 64, 00014 Helsinki, Finland

[3] Radiochemistry Division, Chemistry Department, Lomonosov Moscow State University, Leninskie Gory, Moscow, Russia 119991

[4] Present Address: Center for Radiopharmaceutical Sciences, Paul Scherrer Institute, Villigen, Switzerland

environments iodine is present as iodate (IO_3^-) which is displaced by iodide (I^-) in somewhat less oxidising conditions. In addition to these forms, iodine can be present as molecular iodine (I_2) and different organo–iodine forms including volatile methyl iodide (CH_3I) [13, 14]. The current research interest lies in the verification of the formation and presence of organo–iodine compounds in soils and sediments [12, 15–21]. Irrespective of the initial inorganic chemical form of iodine, the presence of sufficient amounts of organic matter, and especially aromatic carbon, has resulted in the formation of iodinated organic compounds [12, 18, 20, 21], whereas in situations where aromatic carbon content is low, the reduction of iodate to iodide has been observed [18]. The species transformations of iodate and iodide and iodination of organic matter are highly linked to the presence of soil microbes [12, 18, 22, 23].

In addition to the redox potential and chemical form of iodine, factors such as solution composition and pH, soil organic matter content, mineralogy and Al and Fe oxide content bear an influence on the sorption behaviour of iodine [7, 22, 24–27]. Solution pH has a direct effect on the protonation degree of mineral surface hydroxyl groups (M–OH; M = Si, Al, Fe, Mg, etc.) and in the acidic pH values of 2–4, where the maximum sorption of iodine occurs, these groups are in their protonated form ($M–OH_2^+$) [25–29]. When the solution pH increases, the deprotonation of surface functional groups proceeds, which explains the decrease in the sorption of iodine with elevating pH. The most important hydroxyl groups having an impact on the sorption of iodine by ion exchange or surface complexation are those of Al and Fe oxides, which retain their basic character to pH values up to 8, whereas the deprotonation of e.g. Si–OH groups takes place at approximate pHs of 3–4 [27, 28, 30–32]. The mutual contribution of Al and Fe oxides to the retention of iodine depends also on the ambient pH, as at pH values <5 sorption takes place mainly on Fe oxides and at pH 5–7 on Al oxides. However, neither types of oxides can overcome the sorption capacity of organic matter, which exhibits a greater tendency for the retention of iodine in a wide pH range of 3–10 [22, 25, 33].

HPLC is a widely used application for the separation of trace elements into individual components from complex mixtures. Separation into anionic and cationic species, polar and non-polar compounds, and low molecular weight and high molecular weight substances can be achieved by the choice of appropriate separation columns and conditions. When a direct connection between HPLC and ICP-MS is established, the efficient separation of the species is supplemented with on-line quantification at sub parts per million (ppb; $\mu g\ l^{-1}$) level [34]. HPLC–ICP-MS has gained vast popularity in the speciation analysis of iodine from different liquid matrices, such as soil water, groundwater and seawater, with the analytical limit of detection varying from 4.3 ng to 2 $\mu g\ I\ l^{-1}$ [23, 35–37]. In recent years, the development in iodine HPLC–ICP-MS methods has targeted on fast multispecies and multielement separation and identification [38], improving the separation efficiency from complex solution matrices [35, 36, 39] and the use of green eluents (i.e. low salt and organic modifier concentration) [39].

In the present investigation, the sorption and speciation of iodine on humus and mineral soil from the Olkiluoto site was studied by batch sorption experiments. The liquid phase speciation analysis of iodine was carried out with HPLC–ICP-MS. The research aimed to gain insight into the site-specific retention of iodine on Olkiluoto soil and liquid phase speciation changes taking place in the studied soil system. Also, the effect of time, incubation conditions, pH, microbes, temperature and minerals on iodine speciation and sorption were investigated.

Experimental

Soil sampling and characterisation

The sampling site, Olkiluoto Island, is a large island on the coast of the Baltic Sea in southwestern Finland. Here, the final disposal facility for the spent nuclear fuel from the Finnish power reactors is currently being built. To gain on-site information on the speciation and sorption of iodide and iodate, an excavator dug soil pit was sampled from five different depths extending from 0.7 m below the soil surface to a depth of 3.4 m. The soil pit (KK) was encoded as OL-KK20, in which OL refers to Olkiluoto and 20 to the pit number. Aerobic and anaerobic soil samples were collected from each depth and organic humus soil samples were gathered from the vicinity of the soil pit. More detailed information on soil sampling can be found elsewhere [40, 41].

An elaborate discussion on soil characterisation has been previously presented [40–42] and is reviewed here. Soil pH was measured in ultrapure MilliQ water and 0.01 M $CaCl_2$ solution with 1:1 solid to liquid ratio. Soil dry matter content was determined by drying the samples for 24 h at 105 °C and recording the mass loss after the samples were cooled. Organic matter content was measured as loss of ignition (LOI) in sample mass after annealing for 5–6 h at 550 °C in an oven and cooling. Extraction with 1 M ammonium acetate solution buffered to a pH value of 4.5 was applied for the determination of soil cation exchange capacity (CEC) with a solid to liquid ratio of 1:5. Weakly crystalline aluminium and iron oxides were extracted in the dark with a solution of 0.029 M ammonium oxalate and 0.021 M oxalic acid using a solid to liquid ratio of 1:25. Soil mineralogy was examined for grain size fractions of <0.01 mm and 1.0–2.0 mm at the Geological Survey of Finland (GTK) by X-ray diffraction (XRD). The specific surface areas (SSA) of the soil and mineral samples were measured at Chalmers University of Technology with BET/Kr adsorption using Micromeritics ASAP2020 gas analyser instrument.

Determination of iodine sorption in batch experiments

Iodine solutions

Iodine concentration in the percolating groundwater of Olkiluoto soil averages to a value of 5.9×10^{-7} M, whilst the range differs over one magnitude from 7.8×10^{-8} to 1.5×10^{-6} M [43]. The typical chemical form of iodine in Olkiluoto groundwater is unknown, but based on the findings on iodine speciation in soil solution [12, 15, 37], iodide can be assumed to be the dominant species at elevated soil depths. However, it was decided to conduct the experiments with both inorganic forms of iodine, that is iodide ($\mathrm{I(-I)^-}$) and iodate ($\mathrm{I(+V)O_3^-}$).

All the reagents used were of analytical grade (≥98 %). A stock solution containing iodine ($\mathrm{I^-}$ or $\mathrm{IO_3^-}$) at 7.9×10^{-4} M (100 mg I $\mathrm{l^{-1}}$) concentration level was prepared from VWR KI and Merck $\mathrm{KIO_3}$ chemicals by diluting with ultrapure (>18 MΩ) MilliQ water. Iodide and iodate stock solutions were used in all the experiments and synthetic model soil solution (Table 1) was used as the liquid matrix.

Batch sorption tests

Experimental batch sorption tests were conducted by weighing 1.00 g of grain size <2.0 mm sieved soil into a 50 ml Sorvall polypropylene® centrifuge tube. Then 25 ml of synthetic model soil solution (Table 1) and stable iodine either as iodide ($\mathrm{I^-}$) or iodate ($\mathrm{IO_3^-}$) was added at 7.9×10^{-7} M concentration level (0.1 mg $\mathrm{l^{-1}}$ of $\mathrm{I^-}$ or $\mathrm{IO_3^-}$). Each test was done in duplicate except for humus, for which non-sieved samples with a mass of 0.30 g were used, and no parallel samples were done due to the very small overall leftover quantity of the humus material. Additional background blank samples containing only soil and model soil solution were made and treated similarly as the samples containing iodine.

The sample tubes were kept in sample racks on a laboratory table from 1 to 49 days and shaken daily to ensure the thorough mixing of the solid and liquid phases. For humus, the longest incubation time applied was 21 days instead of 49 days. Solution final pH was recorded after the desired incubation time and the tubes were centrifuged for 10 min at 48,400×*g*. The solution was further filtered through a 0.20 µm (Supor®) syringe filter and 1 ml aliquot of the filtered liquid was taken to HPLC–ICP-MS for liquid phase speciation analysis and iodide and iodate concentration quantification. HPLC–ICP-MS measurements were done within 2 days of the phase separation to minimize the possibility of speciation changes induced by the storage. From the results of the concentration measurements, values of distribution coefficients (K_d) were calculated using Eq. 1 for iodide:

$$K_{\mathrm{dI^-}} = \frac{C_{\mathrm{I^-i}} - C_{\mathrm{I^-f}}}{C_{\mathrm{I^-f}}} \times \frac{V(\mathrm{ml})}{m(\mathrm{g})} \tag{1}$$

where $C_{\mathrm{I^-i}}$ is the initial concentration and $C_{\mathrm{I^-f}}$ is the final concentration of iodide in the solution, V is the solution volume (ml) and m is the sample dry mass (g).

In the sorption experiments, a varying fraction of iodate was found to be reduced into iodide. It was necessary to take this into consideration for the K_d calculations of iodate with Eq. 2:

$$K_{\mathrm{dIO_3^-}} = \frac{\left(C_{\mathrm{IO_3^-i}} - C_{\mathrm{IO_3^-f}}\right) - C_{\mathrm{I^-f}}}{C_{\mathrm{IO_3^-f}}} \times \frac{V(\mathrm{ml})}{m(\mathrm{g})} \tag{2}$$

where $C_{\mathrm{IO_3^-i}}$ is the initial concentration and $C_{\mathrm{IO_3^-f}}$ is the final concentration of iodate in the solution, $C_{\mathrm{I^-f}}$ is the final concentration of iodide in the solution, V is the solution volume (ml) and m is the sample dry mass (g).

The respective percentage of iodate reduced into iodide was calculated from Eq. 3:

$$\text{Reduction}\,\% = \frac{C_{\mathrm{I^-f}} - C_{\mathrm{I^-bkg}}}{C_{\mathrm{Ii}}} \times 100\,\% \tag{3}$$

where $C_{\mathrm{I^-f}}$ is the final concentration of iodide in the solution, $C_{\mathrm{I^-bkg}}$ is the iodide concentration in the background samples i.e. extracted from the soil and C_{Ii} is the

Table 1 The chemical composition of the synthetic Olkiluoto model soil solution (mg $\mathrm{l^{-1}}$, mmol $\mathrm{l^{-1}}$) based on the concentration measurements of elements from Olkiluoto soil waters [44, 45]

	Sodium $\mathrm{Na^+}$	Potassium $\mathrm{K^+}$	Calcium $\mathrm{Ca^{2+}}$	Magnesium $\mathrm{Mg^{2+}}$	Chloride $\mathrm{Cl^-}$	Silicate $\mathrm{SiO_3^-}$	Sulphate $\mathrm{SO_4^{2-}}$
mg $\mathrm{l^{-1}}$	4.0	2.7	6.5	2.7	16.5	6.6	10.7
mmol $\mathrm{l^{-1}}$	0.17	0.07	0.16	0.11	0.48	0.09	0.11

iodine concentration added to the samples in the beginning of the experiments.

Batch sorption tests in nitrogen atmosphere

The batch experiments in the nitrogen atmosphere of a glovebox were done by adding 0.6–2 g of soil into weighed 50 ml Sorvall polypropylene® centrifuge tubes. 25 ml of model soil solution and appropriate volume of iodide or iodate solution, all previously equilibrated with the nitrogen atmosphere, were added. Blank samples consisting of soil and model soil solution were done on the side and treated as the samples containing iodine. The samples were kept in sample racks from 1 to 49 days and shaken daily to mix the solid and liquid phases thoroughly. The final solution pH and E_h were measured after the desired time and the solid phase was let to settle down for 0.5–1.5 h followed by filtration through a 0.20 µm (Supor®) syringe filter. Approximately 1 ml aliquot of the filtrate was pipetted into a 1.5 ml glass sample tube for iodine speciation analysis and iodide and iodate concentration measurement with HPLC–ICP-MS. The sample mass recording and HPLC–ICP-MS measurements were done outside the glovebox whereas other stages were conducted within the glovebox. The oxygen level varied depending on the work step but remained below 20 ppm. The carbon dioxide level was steady at 23 ppm throughout the studies.

Effect of pH on iodine sorption

Iodine sorption was studied as a function of pH on a pH scale of 4–9 on mineral soil samples from the depth of 0.7 m. The experimental setup was otherwise identical with the aerobic and anaerobic batch tests, but the solution pH was adjusted to the desired value by adding 0.1 M HCl or 0.1 M NaOH before iodide/iodate introduction. In the aerobic conditions the sample tubes were kept in a reciprocal shaker instead of sample racks. The sample equilibration time was 7 days.

Effect of temperature on iodine sorption

Seven days batch experiments at temperatures of +8, +22 and +38 °C on OL-KK20 0.7 m samples were done in order to gain information on the effect of temperature on iodine sorption. Additional samples were kept in a freezer (−22 °C) for 6 days and left overnight to melt on a laboratory table to simulate the effects of freeze–thaw. Otherwise the experimental arrangement was identical with the aerobic batch tests.

Effect of microbial activity on iodine sorption

Microbe-free samples were prepared by weighing 1.00 g of <2.0 mm sieved soil samples from depth of 0.7 m into a 50 ml centrifuge tube and by thrice heat sterilising them in an autoclave at 120 °C for 20 min. The time between the two first heat sterilisations was 7 days, whereas 3 days waiting time was applied between the second and the third sterilisations. All solutions were filtered through a thrice ethanol washed 0.20 µm syringe filter before use. A 7 day equilibration time was used for the samples and otherwise the experimental setup was identical to that of the aerobic batch tests.

Effect of mineralogy on iodine sorption

Iodine sorption was studied for the typical Olkiluoto soil minerals, i.e. quartz, potassium feldspar, plagioclase, hornblende, chlorite, hematite, muscovite and biotite. A 0.20 g of grain size fraction of mineral sized between 0.075 and 0.30 mm was weighed into a 20 ml vial and 20 ml of model soil solution was added. The solution pH was adjusted to approximately 8 by adding 0.1 M HCl or 0.1 M NaOH. After the pH was stabilised to the desired value, iodide or iodate solution was added to a 7.9×10^{-7} M concentration level and the samples were placed in a reciprocal shaker for 7 days. Otherwise the tests were performed as described for aerobic batch sorption tests.

The plagioclase sample was examined at GTK with XRD and it was found to contain in addition to plagioclase ($Na_{0.622}Ca_{0.368}Al_{1.29}Si_{2.71}O_8$; 78 %) the following mineral impurities: potassium feldspar (8 %), chlorite (4 %), magnesite (4 %), quartz (3 %) and amphibole (3 %).

Determination of iodine speciation with HPLC–ICP-MS

Iodine liquid phase speciation was examined using high performance liquid chromatography (HPLC; Agilent 1260 Infinity) for the separation of the iodine species. HPLC was connected to inductively coupled plasma mass spectrometer (ICP-MS; Agilent 7500 ce) for the online mass sensitive detection of the separated species. HPLC was equipped with Agilent 1260 Infinity quaternary pump and autosampler. An AS11 Dionex anion exchange column (i.d. 4 × 250 mm) and AG11 guard column (i.d. 4 × 50 mm) were used in the separation of iodine species. HPLC and ICP-MS were coupled by the direct connection of PEEK tubing between the column and ICP-MS nebulizer. ^{45}Rh was applied as an internal standard by mixing it continuously with the eluent flow through a T-junction placed between the column and the nebulizer.

The eluent was 15 mM sodium hydroxide (NaOH) with an isocratic gradient and flow rate of 0.8 ml/min. Argon gas was bubbled through the eluent throughout the measurements for the removal of dissolved carbon dioxide. Iodide and iodate were identified against the retention times of known standards. External standards were used in the peak area measurements and production of calibration curves on concentration range of 0–300 µg l^{-1} for the quantification of iodide and iodate. The measured iodine isotope in no-gas mode was ^{127}I (abundance 100 %). The stability of HPLC–ICP-MS was monitored at certain intervals by measuring reagent blanks and a standard with a known iodide and iodate concentration. In the first measurements iodide peak was detected at 551 s, but its retention time increased to 664 s during the three last measurements due to possible column contamination or saturation. Irrespective of this, no extra peaks were detected in the reagent blanks. The increase in the iodide retention time resulted in a lengthening of the total measurement time from 720 to 900 s. The retention time of iodate remained steady at 125 s.

Results and discussion

Soil characteristics

Table 2 presents soil pH, organic matter content, cation exchange capacity, concentration of weakly crystalline aluminium and iron oxides and specific surface areas of the Olkiluoto soil samples. A detailed discussion of the chemical and physical characteristics of aerobic and anaerobic soil samples is given elsewhere [40–42] and this revision focuses on the characteristics of the aerobic soil samples. The characteristics of anaerobic soil samples can be presumed to be similar to the aerobic ones.

The organic matter (OM) rich humus layer had the lowest pH of 4.6 due to the presence of organic matter degradation products and secretions of microbial and plant root origin [40]. The OM content showed a gradual decrease in the mineral soil with increasing soil depth to values <0.5 %, whereas soil pH remained rather constant at 7.0 ± 0.1. Very low potential CEC of 13 $cmol_{(+)}\ kg^{-1}$ was determined for humus. This value was the second lowest among the determined ones, only exceeding the CEC of 6.3 $cmol_{(+)}\ kg^{-1}$ of the highest mineral soil layer at 0.7 m. The highest CEC of 29 $cmol_{(+)}\ kg^{-1}$ was seen at a soil depth of 1.3 m. A systematic decrease in soil weakly crystalline aluminium and iron oxide content from 26 mmol kg^{-1} at 0.7 m to 3.5 mmol kg^{-1} at 3.4 m was noted and attributed to the action of soil forming processes (e.g. hydrolysis and acid reactions) in the superficial parts of the soil [42]. The decrease in the weakly crystalline Al + Fe oxide content was considered to be the main reason for the decrease in soil SSA with depth from 4.3 $m^2\ g^{-1}$ at 0.7 m to 0.38 $m^2\ g^{-1}$ at 3.4 m (Table 2) [42].

Soil mineralogy was dominated by quartz (on average 52 %) at every depth, followed by plagioclase (21 %) and potassium feldspar (19 %) [40]. Kaolinite content was relatively high at 8 % and micas were present in every sample with a <5 % abundance. The minor minerals hematite and amphibole were detected only at the smaller grain size of <0.01 mm. No swelling clay minerals were present [40].

Iodine speciation with HPLC-ICP-MS

Analytical performance of HPLC-ICP-MS

HPLC–ICP-MS has achieved extensive popularity as a speciation analysis method due to its efficient separation of different species by chromatographic means, relatively

Table 2 Chemical and physical characteristics of aerobic Olkiluoto soil samples (n = 2–4 parallel subsamples from each depth) [40, 42]. Soil pH and organic matter content for anaerobic samples can be found elsewhere [41]

Soil depth (m)	pH (1:1 solid to liquid)		Organic matter content ± uncertainty (%)	Cation exchange capacity ($cmol_{(+)}\ kg^{-1}$) ± STDEV	Weakly crystalline Al + Fe content (mmol kg^{-1}) ± uncertainty (%)	Specific surface area ($m^2\ g^{-1}$) ± uncertainty (%)
	In water ± 0.1	In 0.01 M $CaCl_2$ ± 0.1				
0.12	5.3	4.6	14 ± 1	13 ± 3	Not determined	Not determined
0.70	7.9	7.1	0.8 ± 0.3	6.3 ± 2	26 ± 3	4.3 ± 2
1.30	7.8	7.1	0.6 ± 0.1	29 ± 1	8.8 ± 1	1.5 ± 1
2.05	7.7	7.1	0.5 ± 0.1	19 ± 3	5.8 ± 1	0.8 ± 1
3.00	7.7	6.9	0.4 ± 0.1	13 ± 2	3.6 ± 1	0.5 ± 1
3.40	7.8	6.9	0.5 ± 0.1	15 ± 2	3.5 ± 2	0.4 ± 1

high resolution, element specific detection, instrumental sensitivity, repeatability and simplicity of use [34, 35]. For iodine, this method has proved to be a very powerful tool and has been widely used in the simultaneous identification and quantification of inorganic and organic iodine species from differing sample matrices such as rain [46], groundwater and seawater [35, 36, 38, 47], soil extracts [35], soil pore water [37], biological samples [39] and foodstuffs [35].

In our iodine speciation analysis method, anionic iodine species iodide and iodate were separated efficiently with anion-exchange chromatography by a Dionex AS11 separation column and 15 mM NaOH eluent. The linear calibration area of the HPLC–ICP-MS measurements of iodide and iodate standards at the concentration range of 0–300 µg l^{-1} was precise ($r^2 > 0.99$). No matrix-induced extra peaks were detected within the 900 s applied measurement time, as can be seen in Fig. 1 presenting a typical chromatogram for a combined iodide and iodate standard with both species at the 25 µg I l^{-1} concentration level. An iodate peak was detected at 125 ± 1.7 s and an iodide one at 598 ± 55 s. The analytical limit of detection (LOD) for the method by the 10σ criterion (i.e. the standard deviation of reagent blanks × 10) in iodate analysis was 0.30 and 1.51 µg l^{-1} for iodide. These LOD values are within the limits of previously determined ones (0.0043–2 µg I l^{-1}) [12, 35, 36, 38, 39, 47]. As a part of the HPLC–ICP-MS stability verification, a standard containing iodide and iodate at 5 µg I l^{-1} of both species, was measured after 10–15 samples. The measurements yielded 4.81 ± 1.08 µg l^{-1} for iodate and 4.61 ± 1.93 µg l^{-1} for iodide.

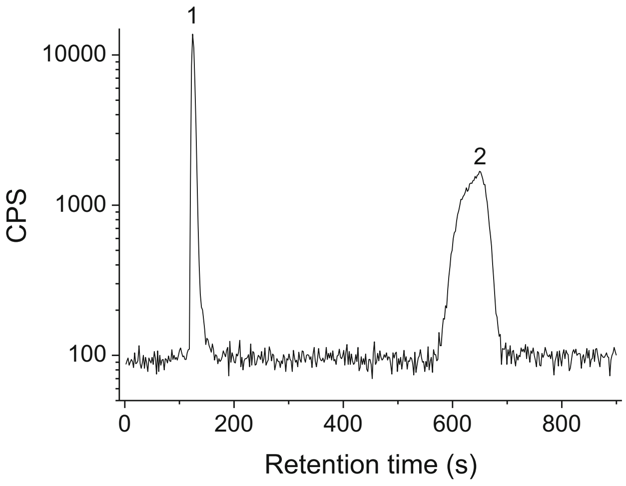

Fig. 1 Iodine HPLC–ICP-MS chromatogram of a mixture of iodate (*1*) and iodide (*2*) standards at 25 µg I l^{-1} concentration level for both species

Change in iodine speciation in model soil solution in contact with soil and native iodine extracted from the soil

Stability of iodide and the reduction of iodate to iodide

Iodide proved to be a rather persistent form in the studied experimental conditions as no formation of iodate was detected in any circumstances consistently with the results of Yamaguchi et al. [12], Kodama et al. [15] and Shimamoto et al. [37]. The observation on the stability of iodide over iodate is further supported by the E_h–pH diagrams of iodine [48], in which the iodide fraction increases with decreasing pH and E_h. Similar results were obtained from speciation modelling with PhreeqC (pH 7–9, E_h +150 − +450 mV) which indicated iodide being fairly stable and dominating form both in aerobic and anaerobic experimental conditions as over 99 % of iodine was present as iodide.

In soils, microbial activity is tightly linked to soil organic matter content as organic matter serves as a nutrient and energy storage medium, source for metabolisable carbon and acts as an electron mediator, source or acceptor for microbe metabolism reactions [12, 49, 50]. Soil microbes have been found to have a positive effect on iodine retention in soils [51–55], and to lead to iodine species transformations [14, 56–58]. For example, Yamaguchi et al. [12] and Evans and Hammad [22] noticed a substantial decrease in the reductive reaction of iodate in sterilised soil. Similar results were obtained in this study, where soil sterilisation yielded a threefold decrease in the reduction of iodate to iodide compared to non–sterilised soil. The respective iodate reduction percentages for sterilised and non–sterilised soil were 0.09 ± 0.02 and 0.33 ± 0.05 %. This result lead us to hypothesize that soil microbes are strongly involved in iodine behaviour in soil.

The reduction of iodate to iodide in humus was 60-fold in comparison with aerobic mineral soil as the respective reduction percentages were on average 37 ± 8 and 0.6 ± 0.7 %. This may have been caused by the enrichment of microbes and their by–products enzymes in the humus layer rich in organic matter. A substantial increase in the reduction of iodate to iodide by a factor of 180 was noticed with temperature increasing from −22 °C (0.19 ± 0.04 %) to +8 °C (34 ± 1 %), which may be linked to an increase in the microbial and enzymatic activity with temperature [15, 59]. Further increase in the temperature from +8 to +22 or +38 °C induced no change in the reduction of iodate as it remained approximately at 34 ± 1 %.

Incubation time had a significant effect on the reduction of iodate in humus as the fraction of iodide increased from 25 % at day 1 to 41 % at day 21. In aerobic mineral soil the influence of time was not as evident since only a 1.4 percentage point increase in the reduction was observed at the end of the 21-day incubation period (Table 3). In anaerobic mineral soil a marked increase in the conversion of iodate to iodide was noticed leading to a value of 24 ± 1 % at day 21 (Table 3). An even higher fraction of 55 ± 4 % was detected on day 49. However, this value is not directly comparable with humus, since the longest incubation period for humus was only 21 days. Nonetheless, the average reduced fraction of iodate in anaerobic soil conditions at the 21-day interval, being 17 ± 19 %, was only 2-times lower than the value determined for humus (37 ± 8 %). Interestingly, soil depth had no systematic effect on the reduction of iodate to iodide both in aerobic and anaerobic soil conditions (Table 3). The instability of iodate in soil environments and its subsequent reduction to iodide has been documented in multiple studies [6, 12, 15, 20, 22, 26, 37, 60, 61], and moderately higher reduction in anaerobic conditions versus aerobic ones have been observed [37, 60]. In humus and aerobic mineral soil the reduction of iodate to iodide is assumed to be a microbe–mediated reduction reaction. However, in anaerobic soil environment abiotic iodate reduction induced by a decrease in the prevailing redox potential and formation of mildly oxidative or reductive soil conditions, is more probable reason for the formation of iodide [20, 37, 60, 62]. It is also possible that the abiotic reduction mechanism acts in humus and mineral soil at least to some degree especially in situations, where microbial activity has consumed all the available oxygen leading to lowered soil oxidation status [13, 15, 52].

Similarly to the results of Fukui et al. [26], pH was observed to have a marked effect on the stability of iodate, both in aerobic and anaerobic conditions. Figure 2 shows the chromatograms measured for aerobic samples at pH values ranging from 4 to 9. The chromatograms for anaerobic soil samples were similar except that peak number 3 was not detected. In aerobic soil environment the decrease in pH from 9 to 4 induced the species transformation of iodate to iodide to increase from 0.02 ± 0.01 to 8.7 ± 0.7 % (Table 4). At pH 5, only 4.4 ± 0.7 % of iodate was reduced to iodide and the fraction decreased further to a rather constant value of 1.2 ± 0.4 % at the pH range of 6–8. The fraction of unreduced iodate increased with pH from 53 ± 1 % at pH 4 to 83 ± 1 % at pH 6 (Table 4). At pH values of 7–9 the fraction of iodate was rather stable at 89 ± 1 % of their initial values. For iodide, our results somewhat differ from those of Fukui et al. [26], as possibly caused by the higher OM content and presumable microbial activity of their samples (2.3 %) in comparison with ours (<1 %). In Fukui et al. [26], the iodide fraction was approximately 5 % at pH 10.6 and about 30 % at pH 3.2, whereas the iodate fraction was at approximately the same level as in our study.

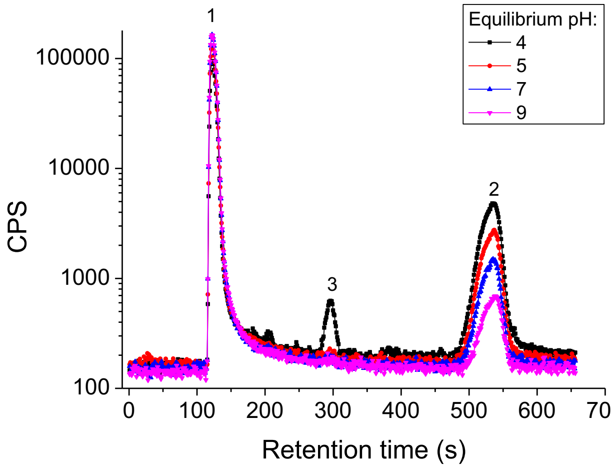

Fig. 2 Chromatogram of iodate solutions contacted with aerobic mineral soil from the sample depth 0.7 m after a 7-day incubation time and adjusted to pH values 4, 5, 7 and 9. From the chromatograms iodate (*1*), iodide (*2*) and an unidentified possible organo–iodine species (*3*) peaks can be clearly distinguished

As in aerobic conditions, pH decrease in anaerobic soil induced increased reduction of iodate (Table 4). The

Table 3 The reduction percentage of iodate to iodide as determined for aerobic and anaerobic Olkiluoto mineral soil at incubation times of 1–49 days

Soil depth (m)	Incubation time (days) IO_3^- reduction %											
	Aerobic soil						Anaerobic soil					
	1	3	5	7	21	49	1	3	5	7	21	49
0.7	0	0	0	0.3 ± 0.1	1.4 ± 0.7	6.9 ± 0.3	0	7.2 ± 2	9.0 ± 3	4.6 ± 0.2	24 ± 1	55 ± 4
1.3	0	0	1.8 ± 0.8	0.8 ± 0.1	8.2 ± 3	2.0 ± 0.3	5.4 ± 5	15 ± 3	31 ± 30	27 ± 1	58 ± 3	73 ± 2
2.05	0.4 ± 0.1	0	1.1 ± 0.4	0.7 ± 0.1	1.9 ± 0.1	2.8 ± 2	3.2 ± 2	7.8 ± 0.3	14 ± 1	16 ± 1	54 ± 6	78 ± 4
3.0	0.03 ± 0.05	0	0.8 ± 0.2	2.0 ± 2	4.5 ± 3	7.5 ± 5	0.2 ± 0.6	11 ± 1	10 ± 1	26 ± 1	31 ± 1	78 ± 2
3.4	0.1 ± 0.1	0	0.5 ± 0.3	0.6 ± 0.4	2.6 ± 2	2.8 ± 1	2.2 ± 1	8.5 ± 0.3	12 ± 1	14 ± 3	45 ± 3	37 ± 4

Table 4 The reduction percentage of iodate to iodide as a function of pH in aerobic and anaerobic soil conditions and the percentage of iodate present from the initial content for aerobic samples

Aerobic soil			Anaerobic soil	
pH	IO_3^- reduction %[a]	IO_3^- present from the added (%)	pH	IO_3^- reduction %[b]
4	8.7 ± 0.7	53 ± 1	4	64 ± 9
5	4.4 ± 0.7	71 ± 1	5	59 ± 9
6	1.3 ± 0.1	83 ± 1	6	42 ± 10
6.5	0.5 ± 0.1	87 ± 1	8	15 ± 8
7	1.6 ± 0.1	88 ± 3	9	10 ± 20
8	1.3 ± 0.5	89 ± 2	9.5	12 ± 8
9	0.02 ± 0.01	90 ± 1		

[a] Calculated from the measured iodide concentration

[b] Calculated from the measured iodate concentration due to high unexplained iodide background level

reduced iodate fraction remained at below 40 % at pH values higher than 6, for example being 9.6 ± 20 % at pH 9. At pH values equal or lower than 6, the reduction percentage of iodate increased to almost 65 ± 9 % at pH 4. In these pH 4–6 soil samples, additional iodide originating from other sources than the reduction of the added iodate or the native iodide extracted from the soil was detected. Measured total iodide fraction ranged from 150 to 190 %, and for this reason it was plausible to calculate iodide fraction as a difference between the iodate fractions in the beginning and at the end of the experiment. More support to this calculation way is given by the absence of unidentified iodine species in the chromatograms. Even if we assume iodate retention to resemble that detected in anaerobic soil conditions after a 7-day incubation (K_d 0.26 ml g^{-1}, Table 5), the error caused to the calculated reduction percentage lies below 2 percentage points. In aerobic soil the K_d value observed at pH 4 was approximately tenfold compared with the K_d of aerobic soil after a 7-day incubation, that is 16 ml g^{-1} (Fig. 4) and 1.7 ml g^{-1} (Table 5). If we assume a similar increase in the K_d value of anaerobic soil from 0.26 to 2.6 ml g^{-1} at pH 4, the error caused to the reduced fraction of iodate would still be less than 10 % points.

Among the investigated minerals, the observed iodate reduction increased in the order of potassium feldspar (0.04 ± 0.04 %), hornblende (0.11 ± 0.2 %), chlorite (0.14 ± 0.14 %), hematite (0.14 ± 0.01 %), biotite (0.38 ± 0.04 %) and plagioclase (0.55 ± 0.2 %), whereas no formation of iodide was detected in the presence of quartz or muscovite. The capability of minerals to induce iodate reduction into iodide seemed to be associated with the presence of structural iron either as Fe(II) (e.g. in biotite) or Fe(III) (e.g. in hornblende and hematite). For potassium feldspar, however, no plausible explanation for the noticed iodate reduction can be given based on its chemical composition of $KAlSi_3O_8$.

All these aforementioned factors combined together imply iodate to be relatively unstable chemical form in the studied soil conditions, which may have tremendous implications on the environmental behaviour of iodine. Increase in soil microbial activity and organic matter content, decrease in pH and development of anaerobic conditions drive the formation of highly mobile and non-retaining iodide.

Formation of possible organo–iodine species

The formation of unidentified clearly distinguishable iodine species from iodate and iodide was detected in organic matter rich humus samples (e.g. peaks 3 and 4 in Fig. 3), but also at lower quantities in aerobic mineral soil samples in the time range of 1–21 days and samples adjusted to pH 4 and 5 (Fig. 2). These unidentified iodine species 3 and 4 are presumed to represent anionic organo–iodine (OM–I) compounds, which can be found and are formed rather universally in soil [12, 15–21].

The formation of organo–iodine compounds in soils requires the presence of reactive electrophilic iodine species such as molecular iodine (I_2) and/or hypoiodous acid (HIO) [21, 61], both of which are unstable forms in the ambient soil environment and are produced by the reduction of iodate [63] and/or oxidation of iodide [64] in the reaction with hydroquinone or semiquinone moieties of organic matter [61] or microbial enzymes [18, 23]. The iodination of organic matter proceeds as a monosubstitution when single proton in ortho- or para-position of preferable aromatic phenol compound is replaced by reactive iodine in enzymatically, peroxidase or metal oxide assisted iodination leading to formation of a strong, covalent C–I bond [16, 18, 19, 25, 65]. The iodination of organic matter favours low-molecular-weight (3–50 kDa) humic compounds [18] and is limited by organic carbon, and especially aromatic carbon, content [17, 18]. The

Table 5 The K_d values of iodide (I^-) and iodate (IO_3^-) determined for aerobic and anaerobic Olkiluoto mineral soils for 1–49 day incubation times

Soil depth (m)	Incubation time (days)											
	Aerobic soil						Anaerobic soil					
	1	3	5	7	21	49	1	3	5	7	21	49
I^- K_d (ml g^{-1})												
0.7	1.0 ± 1	0.5 ± 0.1	1.8 ± 0.4	0.3 ± 0.5	3.7 ± 0.5	4.8 ± 0.5	0	0	1.4 ± 1	0	0	0
1.3	4.5 ± 4	5.6 ± 0.2	1.6 ± 0.1	0.4 ± 0.1	2.0 ± 0.2	7.1 ± 0.9	0	0.8 ± 0.9	3.9 ± 0.1	0.1 ± 0.1	5.2 ± 10	0
2.05	0.4 ± 0.1	0.5 ± 0.1	2.0 ± 0.3	0.6 ± 0.1	1.0 ± 0.2	2.2 ± 2	0	0	7.0 ± 0.3	0.6 ± 0.6	1.0 ± 0.1	0
3.0	1.3 ± 0.3	0.7 ± 0.3	1.8 ± 0.2	0.6 ± 0.2	3.0 ± 0.7	1.0 ± 0.1	7.7 ± 0.2	2.7 ± 4	7.5 ± 3	0.3 ± 0.3	2.0 ± 1	0
3.4	0.4 ± 0.2	1.2 ± 0.9	2.3 ± 0.2	0.6 ± 0.2	1.6 ± 0.1	4.2 ± 2	1.4 ± 0.5	0	3.6 ± 0.2	1.5 ± 2	1.8 ± 0.2	11 ± 7
IO_3^- K_d (ml g^{-1})												
0.7	2.1 ± 0.4	2.3 ± 0.3	2.5 ± 0.1	1.7 ± 0.5	3.0 ± 0.1	7.4 ± 0.5	1.6 ± 0.2	1.2 ± 0.6	2.7 ± 0.3	0.3 ± 0.8	0.3 ± 1	8.0 ± 1
1.3	1.8 ± 0.1	2.0 ± 0.2	1.9 ± 2	0.8 ± 0.1	1.6 ± 0.9	4.8 ± 0.1	0.3 ± 1	1.2 ± 0.3	2.7 ± 0.1	0	0.8 ± 0.7	4.8 ± 0.5
2.05	1.3 ± 0.4	1.0 ± 0.6	1.9 ± 0.2	2.2 ± 1	2.7 ± 0.3	5.2 ± 0.3	0.6 ± 0.1	2.0 ± 0.1	2.5 ± 0.1	0	0.8 ± 0.5	0
3.0	2.9 ± 1	1.1 ± 0.1	0.7 ± 0.4	1.0 ± 0.2	1.9 ± 0.8	7.0 ± 4	1.9 ± 0.4	1.9 ± 0.1	5.0 ± 0.6	0	1.7 ± 0.1	3.6 ± 0.1
3.4	1.1 ± 0.3	0	1.4 ± 0.5	1.2 ± 0.6	2.4 ± 0.9	1.6 ± 0.2	1.0 ± 0.1	1.6 ± 0.2	2.9 ± 0.1	0.2 ± 0.1	1.7 ± 0.1	7.6 ± 2

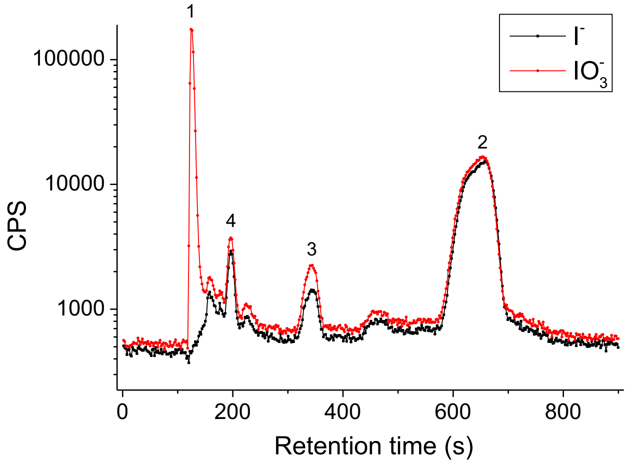

Fig. 3 Chromatogram of iodine solutions in the initial chemical form of iodide and iodate contacted with humus for 3-day incubation time at about pH of 5. From the chromatograms iodate (*1*) and iodide (*2*) can be distinguished. In addition to iodate, iodide and other small peaks, a clear separation of two unidentified and presumed organo–iodine species (*3* and *4*) can be made

presence of sufficient amounts of aromatic carbon results in the iodination of organic matter irrespective of iodate or iodide being the initial chemical form [12, 18, 20, 21], as was also seen in this study. However, in situations where aromatic carbon content is low, the reduction of iodate to iodide has been detected without additional formation of OM–I compounds [18]. This is in line with the results of this study, where the formation of presumed OM–I was accompanied by iodate reduction to iodide from moderate to significant levels.

The presumed OM–I compounds are assumed to present stable forms of iodine since the covalent C–I bond can only be broken to aliphatic chains by stronger nucleophiles and iodine can be replaced by a stronger electrophile [16]. OM–I compounds tend to be easily disintegrated in reducing conditions [16, 23, 52] and this could be the reason why these possible OM–I species were not detected in anaerobic soil samples in any circumstances.

Xu et al. [19] observed iodate to be reduced preferably via the abiotic route by carboxylic–rich alicyclic molecules or tannin– and lignin–like compounds whilst iodide was favourably oxidised by peroxides [19]. This might be a plausible explanation why possible OM–I species 3 was observed in aerobic mineral soil at every soil depth (0.7–3.4 m) with iodide as the initial chemical form, whereas for iodate, possible OM–I 3 was found only at the depths of 0.7–1.3 m.

The presence of possible OM–I species 3 in acidic, pH 4 and 5 samples of aerobic mineral soil can be caused by the formation of soluble molecular iodine in these conditions, even though the presence of I_2 in the samples was not verified experimentally. Also, for these same samples it was observed that over 4 % of the initial iodate was reduced to iodide (Table 4). Iodide, in turn, could have been oxidised to reactive I_2 abiotically by the soil organic matters' quinolic moieties and free radicals [61, 63] or enzymatically by peroxidases [18, 66, 67], all favouring acidic pH ranges [61, 63, 66, 67]. Low solution pH favours the formation of I_2 as observed by Fukui et al. [26], who noticed I_2 fraction to increase from 6 % to over 60 % with pH decreasing from 10.6 to 3.2, when iodide was the initial chemical iodine form. When the starting iodine form was iodate, a rather steady I_2 formation of 6–7 % was observed [26].

In addition to OM–I form, the possibility of species 3 being inorganic tri-iodide (I_3^-) ion needs to be discussed. It is known that I_2 and I^- are in a fast equilibrium with I_3^- by the reaction of $I_2 + I^- \leftrightarrow I_3^-$ [68, 69] and in turn, I_3^- forms a rapid equilibrium with HIO by the reaction of $I_3^- \leftrightarrow 2I^- + H^+ + HIO$ [70]. These reactions would indicate consumption of freshly-formed I_3^- leading to a relatively low concentration in the solution in comparison with iodide. Furthermore, the formation of polyiodides such as I_3^- requires rather high iodide and I_2 solution concentration ($\sim 10^{-6}$ M) [68], which is certainly not met in our samples (initial I^- concentration 7.9×10^{-7} M). For these reasons the likely presence of tri-iodide ion as species 3 can be ruled out.

Native iodine extracted from the soil

Iodide was extracted from all blank samples of humus, aerobic and anaerobic mineral soil irrespective of the incubation time or pH. The highest concentrations were detected in humus, where iodide concentration increased with time from 0.27 µg g^{-1} soil on day one to 0.83 µg g^{-1} soil on day 7 and yielded an average of 0.56 ± 0.20 µg g^{-1}. In addition to iodide, an unidentified possible OM–I species 4 (Fig. 3) was detected in the 21-days blank sample. The concentration of iodate was well below the LOD (0.30 µg l^{-1}) value of the method in all the measured humus and mineral soil samples.

In the aerobic mineral soil blanks, iodide was detected in every sample but its concentration was below the determined LOD value (1.51 µg l^{-1}) of the method. However, the concentration of iodide in the anaerobic blanks twice exceeded the LOD value and averaged to a value of 0.065 ± 0.060 µg g^{-1} soil, which is in line with the water-extractable soil iodine content found in previous studies (0.0064–0.2 µg g^{-1} soil) [71, 72]. Interestingly, variation in solution pH from 4 to 9 had no effect on the extracted iodine concentration neither in aerobic nor anaerobic soil conditions.

The concentration of iodide extracted from soil in anaerobic conditions was eightfold compared to aerobic soil conditions. For anaerobic mineral soil the average pH was almost two pH units higher at 9.50 compared with aerobic mineral soil (7.84). This could have led to a more negative surface charge on the anaerobic mineral soil particles due to the higher deprotonation degree of surface functional groups and subsequent increase in soluble iodide fraction [25, 26, 28, 29]. However, it is more likely that sorbed iodate, typically retained by soils in a greater degree than iodide [15, 26, 60], is reduced to iodide and thus increases the soluble iodine fraction [15, 22, 62].

The concentration of iodide extracted from humus was approximately twofold compared with anaerobic soil and ninefold for aerobic mineral soil. This is caused by the overall of 50-fold (range 13–110) higher iodine content in the organic matter rich Olkiluoto humus layers than in mineral soil [33], induced by the sheer fact that organic matter acts as a principal sorbent for anions in soils causing accumulation in the topsoil layers [24, 25].

Sorption of iodine in soil

Effect of time and incubation conditions

Sorption of iodide and iodate somewhat increased with increasing incubation time on aerobic Olkiluoto mineral soil samples on the studied time range of 1–49 days (Table 5). For example, the K_d value of iodide for soil sample from the depth of 0.7 m was 1.0 ± 0.3 ml g^{-1} on day 1 and reached a value of 4.8 ± 0.5 ml g^{-1} on day 49. The respective K_d values for iodate with the same incubation times and sampling depth were 2.1 ± 0.4 and 7.4 ± 0.5 ml g^{-1}. The overall retention of iodate was on average 1.9-times higher than that of iodide. The increase in the retention of iodine with incubation time has been previously observed [7, 22, 26, 54, 73, 74], and is considered to be due to the molecular diffusion of iodine into inner spaces of particles and retention within [26, 54]. The range of K_d values (0–7.7 ml g^{-1}) determined for iodide and iodate are within the limits of previously reported values (0–140 ml g^{-1}) [26, 29, 54, 73–77].

The sorption of iodide and iodate differed only very little between aerobic and anaerobic incubation conditions. On average, slightly better retention was observed in aerobic soil conditions as indicated by the 1.3–times higher K_d values for iodide and 2.5-fold for iodate. For example, the average iodide K_d at 1–49 days incubation times for sample at the depth of 1.3 m in aerobic conditions was 3.5 ± 1.4 ml g^{-1}, whereas the respective value in anaerobic soil was approximately half of it at 1.7 ± 6.0 ml g^{-1}. For iodate, the respective values were 2.1 ± 0.4 and 1.4 ± 1.0 ml g^{-1}. Rather surprisingly, in anaerobic soil the K_d values for iodide were on average 3.3-times higher than the respective ones for iodate.

Iodine sorption in aerobic and anaerobic conditions has been thoroughly discussed in the literature. The consensus is that there is better retention in well-aerated environments as observed in previous studies [37, 52, 62, 75, 78]. The decrease in the retention in reducing soil conditions is typically attributed to the desorption of iodide from soil surfaces and more preferentially, the reduction of sorbed iodate to iodide and subsequent increase in solution iodine concentration due to the more soluble nature of iodide [15, 37, 62, 78]. Support for this hypothesis was received from our speciation studies, where the fraction of iodate reduced to iodide increased from 0 % on day 1 to 24 % on day 21 and reached even 55 % on day 49. Furthermore, higher amounts of native soil iodine were extracted in anaerobic conditions versus aerobic ones, 0.66 and 3.19 μg l^{-1}, respectively. The increased reduction of iodate was further supported by the lower average E_h measured in iodate solutions, being $+118 \pm 40$ mV, compared to the average value of $+170 \pm 75$ mV for iodide. Solution pH remained steady at 9.5 ± 0.3 irrespective of iodine species or incubation time.

The retention of iodine showed only a slight variation with soil depth both in aerobic and anaerobic soil conditions and is believed to be affected by changes in soil OM content, weakly crystalline Al + Fe oxide content, SSA and pH [24–26, 32, 54].

Sorption on humus

The average iodide K_d for humus was approximately 4–times higher than the corresponding value for aerobic mineral soil from the depth of 0.7 m with 1–21 day incubation times, averaging to a value of 8.8 ± 15 and 1.4 ± 1.2 ml g^{-1}, respectively. Iodide K_d values for humus showed no systematic increase with time, even though the highest value of 39 ml g^{-1} was observed on day 21. For iodate, the difference between humus and mineral soil K_d values was over 20-fold as the values averaged to 53 ± 79 and 2.3 ± 0.5 ml g^{-1}, respectively. A systematic increase in iodate K_d values on humus from 0 ml g^{-1} on day 1 to 210 ml g^{-1} on day 21 was observed. The results indicate significant iodine retention on OM rich soil layers in comparison with mineral compartment, which is very well in line with previous findings for iodine accumulation in Olkiluoto humus and mineral soil [33] and peat [51]. Iodine K_d values on humus were at the lower limit of previously reported ones for iodide by Muramatsu et al. [77] (8–581 ml g^{-1}) and Söderlund et al. [75] (9.6–230 ml g^{-1}), for iodate by Muramatsu et al. [77] (10–86 ml g^{-1}) and for iodine by Sheppard and Thibault [76] (1.4–368 ml g^{-1}). It is probable that the difference between the K_d values reported in the literature [75–77] and our study arises from the relatively high iodine concentration of 7.9×10^{-7} M used in this work.

The importance of organic matter for the retention of iodine in soils and wetlands has been observed in multiple studies [22, 24, 25, 51, 79] and is classically explained by the variety of soil organic matter's functional groups participating in the sorption reaction at pH values ranging from acidic to slightly basic [22, 25, 28, 54]. However, soil organic matter has been shown to affect iodine not only by means of sorption, but to also induce a change in its speciation by the formation of organo–iodine compounds [12, 15–21]. These OM–I compounds are found to exhibit much greater and stronger attraction towards mineral phases than inorganic iodine forms iodide and iodate [23]. Also, observations of OM–I compounds comprising the majority of iodine fraction retained by mineral phases have been made [12, 15, 20, 23]. In the liquid phase speciation analysis of humus samples, the formation of possible OM–I compounds was observed (see Fig. 3), thus supporting the hypothesis of iodine retention as OM–I compounds.

Effect of pH

No retention of iodide or iodate was detected on anaerobic Olkiluoto mineral soil at any given pH in the 4–9 pH range. In aerobic soil conditions the sorption of iodide and iodate showed a systematic decrease with increasing pH (Fig. 4). For iodide, the decrease was from 10 ml g^{-1} at pH 4.1 to 2.5 ml g^{-1} at pH 9.2. The retention of iodate decreased from 16 ml g^{-1} at pH 4.0 to almost identical K_d values with iodide at pH 6 and higher (Fig. 4). Similarly to our results, the retention of iodine on soil, minerals and peat has been established to decrease with increasing pH [7, 25–27, 51].

The increase in the possible I_2 formation with decreasing pH in iodide solutions, as observed by Fukui et al. [26],

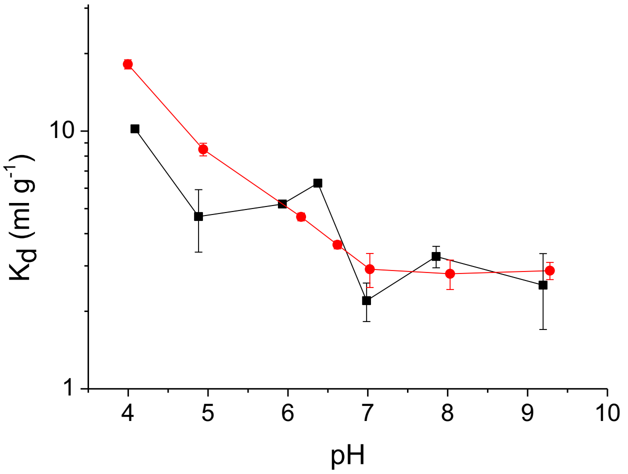

Fig. 4 The K_d values of iodide (*squares*) and iodate (*circles*) on aerobic Olkiluoto mineral soil from the sample depth 0.7 m as a function of solution equilibrium pH

may have induced the higher retention of iodine at pH 4–5 by the formation of possible OM–I compounds (peak 3 in Fig. 2). Also, solution pH can bring about the change in the surface charge of soil particles. The maximum sorption of iodine has been found to take place at the slightly acidic pH values of 2–4 [7, 25–27, 29, 51], in which most minerals exhibit positive surface charge due to protonation of amphoteric surface functional groups into M–OH_2^+ (M = metal) form [28]. With increasing solution pH, the surface charge reaches neutrality when the concentrations of protonated and deprotonated (e.g. M–O^-) functional groups are equal, and turns negative with the deprotonated forms overcoming the protonated ones. Of the functional groups present on soil particle surfaces, Al–OH and Fe–OH are considered as to be highly important due to their weak acidity and tendency to deprotonate at elevated pH values (pK_a of 8) [28]. These properties make Al–OH and Fe–OH important functional groups also for ion exchange reactions and surface complexation by ligand-exchange mechanism of anions even in pH neutral solutions, where the overall impact of Si–OH groups is non-existent due to the tendency to deprotonate in slightly acidic pH environments (pK_a of 3–4) [28].

As the sorption mechanism of iodide, and mainly also of iodate, is ion exchange [7, 27, 30, 74, 80], their retention as charge compensating anions by outer sphere complexation or in the diffuse ion swarm is susceptible to competition of other anions in the solution [27, 29, 74, 80]. However, it has also been proposed that iodate is retained by surface complexation on surface Al and Fe atoms [31, 32] but this tends to be weak as iodate is easily replaced by more strongly basic oxyanion ligands (weaker acids), for example HPO_4^{2-} [80].

Effect of temperature

Iodate retention showed no dependence on the temperature in the studied temperatures of −22, +8, +22 and +38 °C. The K_d value ranged from 0.48 to 0.80 ml g^{-1} and averaged to 0.57 ± 0.14 ml g^{-1}. For iodide, the K_d values were 0 ml g^{-1} at the temperatures of +8, +22 and +38 °C, whereas at −22 °C considerably high retention was observed as the K_d reached a value of 6.1 ml g^{-1}.

Quite similarly to our results, Fukui et al. [26] observed no systematic trend between temperature and the sorption of iodide. The K_d values were slightly higher than in our study, as they ranged from 2.2 to 4.0 ml g^{-1} [26]. In the same study, iodate retention was found to decrease with increasing temperature: at +15 °C K_d had a value of 20 ml g^{-1}, which decreased to 4.2 ml g^{-1} at +55 °C. However, no explanation for the observation was given. Recently, Lusa et al. [51] showed iodide sorption to exhibit dependence on the temperature in their experiments with peat. Sorption was favoured at +20 °C in comparison with +4 °C, which was explained by an increase in the kinetic energy of the molecules and increased enzymatic activity affecting iodide oxidation and incorporation into organic matter. The absence of temperature dependence for our samples, however, can be caused by the low organic matter content (<1 %), overall low sorption of iodide and iodate on Olkiluoto mineral soil and indicate the participation of soil inorganic components in the retentive processes rather than soil microbes.

Effect of microbes

Soil sterilisation to remove microbiological activity had no effect on the retention of iodide or iodate on Olkiluoto mineral soil from the depth of 0.7 m. Iodide showed no sorption either in non-sterilised or sterilised soil samples with a 7-day incubation time. Iodate K_d value remained approximately the same, being 1.7 ± 0.5 ml g^{-1} in non–sterilised soil and 2.2 ± 0.8 ml g^{-1} in sterilised soil. These results are quite contrary to previously determined ones [22, 32, 51, 54, 55, 73, 77], where reduction in soil microbial activity induced a considerable decrease in the retention of iodine. The effects of soil microbes and their by–products enzymes have been proposed to affect iodine through the reduction of iodate and/or oxidation of iodide into electrophilic I_2 and HIO moieties [63, 64] before their abiotic or microbial assimilation into organic matter [18, 61] or possible incorporation into bacterial cells [51].

Our results indicate that soil microbes only play a minor role in the direct retention processes of iodide and iodate in organic matter poor mineral soil and that soil abiotic, mineralogical compartment assumes more importance in the sorption reaction of iodate. However, one has to keep in mind that the formation of possible OM–I compounds observed in aerobic mineral soil samples was considered to be caused by the action of microbes and/or enzymes and thus their absence may have a marked effect on the speciation and environmental behaviour of iodine.

Effect of mineralogy

The retention of iodide and iodate was studied on eight Olkiluoto soil minerals, namely quartz, potassium feldspar, plagioclase, hornblende, hematite, chlorite, biotite and muscovite. From these minerals only muscovite exhibited sorption for iodide in the model soil solution at about pH 8 with a K_d value of 12 ml g^{-1}. Muscovite also proved to retain iodate best (K_d 19 ml g^{-1}), followed by biotite (14 ml g^{-1}), chlorite (9.6 ml g^{-1}) and hematite (1.4 ml g^{-1}). These values are within the range previously reported for chlorite [27, 31], biotite [81] and hematite [31].

Sorption reaction typically exhibits dependence on grain size. Since all the minerals used in this study were sieved into the same grain size fraction of 0.075–0.3 mm, the correction of the determined K_d values by their specific surface areas (Table 6) was plausible. The SSA corrected K_d value, namely K_a, allows the comparison of the sorptive properties of minerals towards iodine excluding the effects of variations in their inner and outer SSA [40]. The highest K_a value was for chlorite at 16 ml m^{-2}, this was followed by biotite (12 ml m^{-2}), hematite (9.7 ml m^{-2}) and muscovite (7.1 ml m^{-2}). The SSA of biotite and muscovite is presumed to consist mainly of inner surface area [42]. The rather low K_a values of these minerals indicate that in spite of their large SSA, their surface functional groups show smaller selectivity towards iodine than those on hematite or chlorite.

Soil minerals have been reported to show variable retention of iodine. Typically higher sorption is attributed to the presence of Fe(II) in mineral phases, such as in pyrite and biotite, leading to reduction of iodate to I_2 or I^- [8, 81]; the occurrence of metal ions capable of forming insoluble metal iodides like in cinnabar [82]; or the replacement of H_2O or –OH ligands at hydrous surfaces or exposed edges found in weakly crystalline iron and aluminium oxides and chlorite [31]. Respectively, quartz has been shown to present no or minimal sorption of iodine [27], probably caused by the acidic silanol (Si–OH) groups on its surface being unsusceptible to anion exchange reactions [28]. Thus, it is plausible to presume that the noted sorption of iodate on chlorite, muscovite and hematite was caused by specific sorption via a ligand exchange mechanism on the surface Al or Fe atoms, whereas in biotite the sorption took place due to the reductive role of structural Fe(II). However, when considering the possible roles of each mineral in the Olkiluoto soil, it is assumed that muscovite and weakly crystalline aluminium and iron oxides (precursors for crystallised Al and Fe oxides) as inorganic sorbents are mainly responsible for iodine owing to their relatively high abundance in comparison with other retentive minerals [40, 42].

Conclusions

Iodine sorption and speciation in the initial chemical form of iodide and iodate was studied in batch experiments on humus and mineral soil samples collected from a boreal forest soil excavator pit on Olkiluoto Island in Finland. The HPLC–ICP-MS technique was used to investigate the possible species transformations of iodine and to quantify the concentration of iodide and iodate in the samples. Increase in soil depth accompanied by an increase in soil pH, decrease in OM matter content and soil redox potential, lowered iodide and iodate soil retention (maximum K_d values ≤11 ml kg^{-1}). Humus layer having the highest microbial activity, presented the best retention of inorganic iodine species (ave I^- K_d 8.8 and IO_3^- 53 ml kg^{-1}) which can be partly caused by formation of the observed unidentified, presumed organo–iodine compounds in probable microbe–mediated assimilation processes. These compounds were detected in aerobic soil samples of low pH (4–5) and of different incubation times. The presumed OM–I compounds were formed with iodide and iodate being the initial iodine form. No presumed OM–I compounds were detected in anaerobic soil conditions. Iodide seems to be rather persistent towards oxidation into iodate, since no evidence of such a reaction was obtained. Iodate is considered very unstable form in versatile soil conditions. Its reduction into iodide increased with time; formation of anaerobic soil conditions; presence of humus; and increased microbial activity and temperature. Iodate was slightly better retained by soil components than iodide, but the overall retention of both species was small. When considering a radioactive iodine plume arriving in the regolith from soil–bedrock interface, it is anticipated that iodine as iodide will diffuse upwards in a soil profile through the reducing soil layers without major interactions with mineral phases. At slightly oxidative soil layers with sufficient OM content part of iodide can be converted into OM–I compounds, which exhibit higher retention tendency towards mineral phases than iodide, thus leading a fraction of iodine to exit the solution phase. Upwards in a soil profile the formation of OM–I compounds, and simultaneous sorption of inorganic and organic iodine forms,

Table 6 Specific surface areas of the selected minerals [42], iodide and iodate K_d (ml g^{-1}) values and surface area corrected distribution coefficient values (K_a; ml m^{-2}) in model soil solution as determined at about pH 8

Mineral	SSA (m^2/g)	I^-		IO_3^-	
		K_d (ml g^{-1})	K_a (ml m^{-2})	K_d (ml g^{-1})	K_a (ml m^{-2})
Hematite	0.14	0	0	1.4	9.7
Chlorite	0.60	0	0	9.6	16
Biotite	1.2	0	0	14	12
Muscovite	1.4	12	4.7	19	7.1

No sorption took place on quartz, potassium feldspar, plagioclase or hornblende increases with increasing soil redox potential, OM content and microbial activity and decreasing pH, eventually being the highest in OM rich humus layer. Also, especially in this OM rich soil layer other effects of microbial origin (e.g. bioaccumulation, biosorption) can be of great importance. The fraction of OM–I compounds will most probably increase with time and possibly lead to circulation and containment of radioactive iodine in the humus layer.

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