Sorption of iodine in soils: insight from selective sequential extractions and X-ray absorption spectroscopy

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Sequential extraction of iodine from German reference soils and speciation with X-ray absorption spectroscopy

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Highlights:
- German reference soils provide little sorption for high amounts of iodine.
- Risk of migration is increased especially for iodate due to low sorption.
- Reduction of iodate to intermediate species or iodide increases sorption.
- High risk is given when iodate is applied to soils containing little organic matter.
- Speciation proves secondary long time reactions to take place for iodate.

Keywords:
Iodine
Migration
RefeSol
Sequential extraction
Speciation
XAS

Abstract

Concerning risk assessment after release of radioactive isotopes, detailed information on sorption and migration behavior of radionuclides in soils is required. The amount of soil organic matter has a distinctive influence on sorption processes. Sorption capacity of different soil types was examined in batch experiments using four reference soils from Germany for short (1 day, 30 days) contact time. Furthermore, sequential extraction was used to characterize the binding of iodine to different soil components. 73 to 96% of the applied iodide were adsorbed within the first 24 hours of contact time, whereas iodate showed little adsorption (11 to 41%), unless contact time was increased (62 to 85%). The organic fraction proved to contain most of the adsorbed iodide and iodate. However, after short contact time 42 to 67% of adsorbed iodate was desorbed easily by extraction with deionized water and buffer solutions, and distinct time dependence could be observed. XAS results reveal rapid change of iodide into organo-iodine when exposed to soil, while iodate did not show a change in speciation. Migration behavior of both iodine species has to be

considered as iodide appears to be the less mobile species due to fast binding to soil organic matter, but with the potential risk of mobilization when oxidized to iodate.

1. Introduction

One result of nuclear accidents, as happened in Chernobyl and Fukushima, is the release of radioactive material into the environment. When ^{235}U is used as nuclear fuel, different iodine isotopes are produced during the fission process, for example ^{129}I (0.841 %) and ^{131}I (2,878%). The short-lived isotope ^{131}I (half-life: 8.02 days) with a specific activity of 4.6 $TBq*g^{-1}$ proves to be highly dangerous and is responsible for high doses when inhaled or ingested after accidental release. Dose commitment to the thyroid is fairly high and enhances the risk of radiation damages, for instance thyroid cancer (Cardis et al., 2005).
^{129}I, in contrast is considered less dangerous due to its long half-life ($1.57 *10^7$ years) (Kocher, 1981) However, when assessing deep geological repositories for radioactive waste for time spans of 100000 years or more, ^{129}I might not only become relevant but also in some scenarios be even the dose determining radionuclide (Lee et al., 2007; Watkins et al., 1999). A possible leakage scenario from an underground repository can lead to at least local contamination with significant activities caused by ^{129}I due to migration processes. Low sorption capacity of soils contributes to migration of iodine into ground and drinking water and transfer into the biosphere. In order to perform a risk assessment, distribution of iodine in soil for low concentrations and for different species has to be investigated.

First iodine analyses in soil were performed in the 1970's and results indicated a correlation between iodine adsorption and amount of organic substance found in soil (Whitehead, 1973, 1978). Destruction of soil organic matter from soil, as well as removal of metal oxides leads to reduced iodine sorption. Various soil types were analyzed by Muramatsu (1989) and sandy soil types were proved to sorb less iodine compared to andosols with low organic matter content. Right after the Chernobyl accident, studies by Lieser (1989) indicated that inorganic components in sediments do not provide sorption sites for iodine, however, organic substances in carboniferous particles and microbial activity enables iodine sorption in investigated sediments. Iodine sorption is increased via iodination of organic matter by microorganisms (Schwehr, 2009). Influence of microbial activity lead to changes in iodine species, not only in soil, but also in seawater. Oxidation of iodide to molecular iodine (I_2) and also to diiodomethane and chloroiodomethane are possible reaction pathways when iodide-oxidizing bacteria are present (Amachi et al., 2005). Xu et al. describe the strong binding of iodine to SOM at Savannah River Side with the conclusion that iodine sorption processes as well as the found iodine species are concentration dependent (Xu et al., 2011; Xu et al., 2012). Hansen et al. underlined the important role of natural organic matter, such as humic acids, fulvic acids and humin, for the binding process of iodine in soil (Hansen et al., 2011). Binding of iodine to organic matter appears to be the predominant mechanism, though

differences between applied iodine species have been highlighted (Schwehr et al., 2009; Zhang et al., 2010).

However, as there are many different oxidation states of iodine (it can exist as –I, 0, I, V, VII), behavior at different natural conditions is rather difficult to predict. Numerous investigations focused on the influence of different iodine species on soil sorption. Yoshida et al. (Yoshida et al., 1992) demonstrated that desorption of iodate (V) from metal oxides is possible. (Dai et al., 2004) differentiated on one hand a positive correlation between metal oxides in soil and iodate sorption, on the other hand a negative correlation for soil organic matter.

Under most natural conditions, the prevalent iodine species should be iodide (see Pourbaix-digram in (Tigeras et al., 2011)). In nature, iodine can also be present in its oxidized form iodate (Kaplan et al., 2014). A study by (Shetaya et al., 2012) considered the oxidation and reduction processes as key for iodine sorption. Oxidation of iodide and reduction of iodate lead to intermediate products, for instance molecular iodine (I_2), triiodide (I_3^-), and hypoiodous acid (HIO) (Jammoul et al., 2009; Xu et al., 2011). Direct proof for organo-iodine formation was given by Shimamoto et al. (2011) with the help of XANES and EXAFS experiments. Currently performed experiments indicate that iodate is the predominant species as which iodine is released from nuclear reprocessing plants into the ocean, thus, our investigation is targeting both iodide and iodate.

In order to elucidate some integral questions concerning migration behavior of iodine in different soil types, sorption and extraction experiments were performed. Hou, Luo and Hansen (Hansen et al., 2011; Hou et al., 2003; Luo et al., 2013) investigated iodine speciation in soils and sediments from Belarus, China, Denmark, Russia, and Sweden. With similar techniques, for instance sequential extraction, we investigate iodine sorption behavior in so called RefeSol soils, representative for soils found in Germany.

Up to now, only few researchers have addressed the investigation of radionuclide distribution in RefeSol (Hormann and Fischer, 2013) with iodine not being investigated at all. This generic approach makes allowance for the fact that no specific site for a nuclear waste repository in Germany has been defined yet, however, iodine need to be understood for safety assessments.

Traditionally sequential extraction is performed with natural soil and sediment samples, respectively, which exhibit long contact times of ^{129}I to soil. As time appears to be an important factor regarding iodine sorption, due to high mobility of iodine in soil when dissolved in water, this paper focusses on the effect of short time contact of iodine with soil. We present analyses of extraction patterns after short contact times, in order to investigate possible contamination from repositories or nuclear accidents.

2. Materials and methods

2.1 Sample preparation

Batch experiments on iodine sorption were performed using four different reference soils (RefeSol 1, 2, 3, 4). The RefeSol system consists of topsoil material (0 – 30 cm) from farmland and grassland, respectively, representing typical soil types under agricultural use in Germany. The preconditioned soil material (air dried and sieved to <2mm) is provided by Fraunhofer Institute for Molecular Biology and Applied Ecology (Fraunhofer IME) and the German Environmental Agency (UBA). In Table 1 significant soil characteristics as analyzed by the Fraunhofer IME are displayed. Furthermore, ICP-MS measurements were performed to determine total iodine concentrations of the soils.

RefeSol 1 and 4 are sandy soils with 76.7 % and 82.7 % sand content, respectively. RefeSol 2 and 3 show a lower sand amount but higher amounts of slit and clay. RefeSol 3 and 4 contain the highest amounts of organic carbon (C_{org}) with 3.05 % and 2.79 %, respectively, while RefeSol 1 and 2 contain less than 1 %. All of the RefeSol soils exhibit pH-values between 5.2 and 6.6, which reflects the slightly acidic character of the majority of soil types in Central Europe.

Table 1: Soil characteristics as analyzed by Fraunhofer Institute for Molecular Biology and Applied Ecology (IME), and iodine content in mg kg^{-1} (=ppm) by ICP-MS.

	sand [%]	silt [%]	clay [%]	pH ($CaCl_2$)	C_{org} [%]	N [g/kg]	CEC_{eff} [mmol kg^{-1}]	Iodine content [ppm]
RefeSol 1	76.7	17.2	6.10	5.33	0.80	0.71	17.9	0.69
RefeSol 2	2.30	82.0	15.7	6.63	0.98	1.25	53.4	0.84
RefeSol 3	17.7	57.5	24.8	5.91	3.05	3.57	73.5	1.81
RefeSol 4	82.7	12.7	4.60	5.22	2.79	1.41	37.3	0.79

Soil samples (4.0 g) were weighed into 50 ml polyvinyl chloride centrifuge tubes and dispersed in 35.6 ml of 10^{-2} M $CaCl_2$ solution establishing an ionic strength similar to natural soil solution. 4.0 ml of 10^{-7} M iodide or iodate solution prepared with KI and KIO_3 (p.a., Merck, Sigma Aldrich), respectively, was added as inactive carrier for iodine. Subsequently, 0.4 ml of $^{125}I^-$ and $^{125}IO_3^-$-solution, respectively, was used as radioactive tracer. Specific activity did not exceed 0.2 MBq per milliliter. The resulting mass/volume ratio of the samples was 1:10. After preparation, samples were placed on a horizontal shaker and incubated for 1 and 30 days at room temperature, respectively. Homogenous mixing was ensured by repeatedly turning the vials.

^{125}I has a half-life of 59.4 d and a low energy gamma line at 35.5 keV with an emission probability of 6.6 %. Tracer activity was determined employing a NaI detector, keeping the geometry of all of the samples constant. Calculation of the sample activities was carried out by measuring reference solutions of known activity. From these results the relative sorption is calculated, which is the percentage of added adsorptive actually adsorbed by the soil matrix.

2.2 Sequential Extraction

After incubation, solid and liquid phase were separated by centrifugation at 3000 rpm for 30 minutes and the supernatant was discarded. Sequential extraction was performed according to the scheme in Table 2. Fractions were chosen following the method described by Luo et al. (Luo et al., 2013) introduced for iodine extraction with minor changes: (1) a water soluble phase was chosen as first extraction step and (2) the last step (combustion) was replaced with direct measurement of remaining ^{125}I-tracer in soil. The leaching solution was prepared and kept in contact with soil samples at a specific temperature for a fixed time interval. Extraction steps requiring room temperature were performed on a shaker; for heating a water bath was used, and manual shaking was performed in defined intervals. The leachate was decanted from the soil and 1 ml of the solution was used for measurement. Washing solutions were prepared and measured likewise. The residual soil was exposed with the successive extracting agent for the next extraction step. Below a detailed procedure of the sequential extraction is shown:

Step 1: Water soluble phase: 40 ml of deionized water was added to prepared soil sample; batch vials were shaken for 2 hours at room temperature.

Step 2: Exchangeable phase and carbonates: 40 ml of 1.0 M ammonium acetate (NH_4Ac) was added to the residual soil sample from step 1; batch vials were shaken for 2 hours at room temperature.

Step 3: Organic fraction: 40 ml of 10^{-2} M sodium hydroxide (NaOH) was added to the residual soil sample from step 2; batch vials were placed in a water bath heated to 80 °C for 6 hours. Manual shaking was performed every 60 minutes. Centrifugation took place directly after removing the batch vials from the water bath.

Step 4: Metal oxide fraction: 40 ml of $4.0*10^{-2}$ M hydroxylamine hydrochloride $(NH_3OH)_2*HCl$ was added to the residual soil sample from step 3; batch vials were placed in a water bath heated to 80 °C for 6 hours. Manual shaking was performed every 60 minutes. Centrifugation took place directly after removing the batch vials from the water bath.

Table 2: Sequential extraction procedure with used chemicals and parameters.

Extraction steps	Extracting agent	Temperature (°C)	Contact time (hours)	pH	Dissolved fraction
Step 1	H_2O (dest.)	RT	2	soil	water soluble iodine
Step 2	1 M NH_4Ac	RT	2	7	exchangeable iodine

Step 3	0.3 M NaOH	80	6	14	iodine bound to organic
Step 4	0.04 M $NH_2OH*HCl$	80	6	3	iodine bound to metal(-oxides)

2.3 X-ray absorption spectroscopy

Iodine K-edge XAFS spectra have been measured at The Rossendorf Beamline (BM20) at the ESRF (Grenoble France). The synchrotron beam was monochromatized by using a water-cooled Si(111) double monochromator. The beam was collimated onto the monochromator by a 1.4 m long, longitudinally bent, Pt-coated silicon mirror. Higher harmonics were suppressed by this mirror and an additional 1.3 m long toroidal mirror also coated with Pt. The XAFS spectra were collected in fluorescence mode using a 13 element high-purity Ge detector (Canberra) with a digital spectrometer (XMap XIA). Samples were cooled to 12 to 15 K with a closed-cycle He cryostat during the measurements to suppress thermal vibrations of atoms and to prevent beam- and oxygen-induced changes of the iodine oxidation state. Several spectra were collected, corrected for energy and fluorescence deadtime and averaged using the SixPack program suite (Webb, 2006). Data reduction and shell fitting was done using standard routines in WinXAS (Ressler, 1998). Theoretical phase shift and amplitude functions were calculated with FEFF8.4 (Ankudinov and Rehr, 1997) based on model clusters of KI, KIO_3 and 1-Iodo-2,3,5,6-tetramethylbenzene (Cortona, 1992; Hamdouni N., 2012; Lucas, 1985)

Soil samples were treated with iodide and iodate, respectively. Contamination of soil was performed as shown in *2.1 Sample preparation*; a detailed sample list can be found in Table 3. In order to achieve time resolved sorption behavior, different contact times were used for iodide. For contamination with iodate, different batch conditions were examined. Sample preparation for XAS experiments were performed at room temperature. Preliminary tests proved that concentrations of added iodine solution lower than 10^{-4} M result in poor signal-to-noise ratio. Increase of measurement time would not lead to intended improvement of signal quality. Therefore, for XAS measurements iodine solution concentration was set to 10^{-2} M for both iodide and iodate solution, respectively.

Table 3: Prepared samples for XAS-measurements, contamination time and further treatment of soils.

Sample No.	Contact time [d]	Iodine species	Additional experimental conditions
P1	1	KI	---
P2	5	KI	---
P3	20	KI	---
P9	20	KIO_3	---

P11	20	KIO_3	Sterilization process
P12	20	KIO_3	Air dried after contamination

3. Results

3.1 Sorption capacities

The results of the sequential extraction after addition of iodide and iodate are presented in Figure 1 – 3, respectively.

After 24 hours contact time only small amounts of iodate are adsorbed (Fig. 1). Less than 12, 15, 18, and 41 % of the iodine from the 10^{-7} M solution is adsorbed after one day contact time for RefeSol 1 to 4. As expected, RefeSol 1 and RefeSol 2, which are poor in organic matter, show little sorption of iodate after short contact time. Concerning the assumption that an increasing SOM content of the soil enhances iodate sorption the results for RefeSol 3 and 4 seem to be contradictory. However, after a contact time of 30 days iodate adsorption displays good correlation with the corresponding SOM content in all cases. RefeSol 1 showed the highest increase from 24 % to 62 % of added iodate; RefeSol 3 had the greatest sorption capacity with 85%.

In contrast, adsorption of iodide on all of the soils examined exceeded the total iodate adsorption already after a contact time of 24 h: iodide is adsorbed much faster and to a higher extent than iodate.

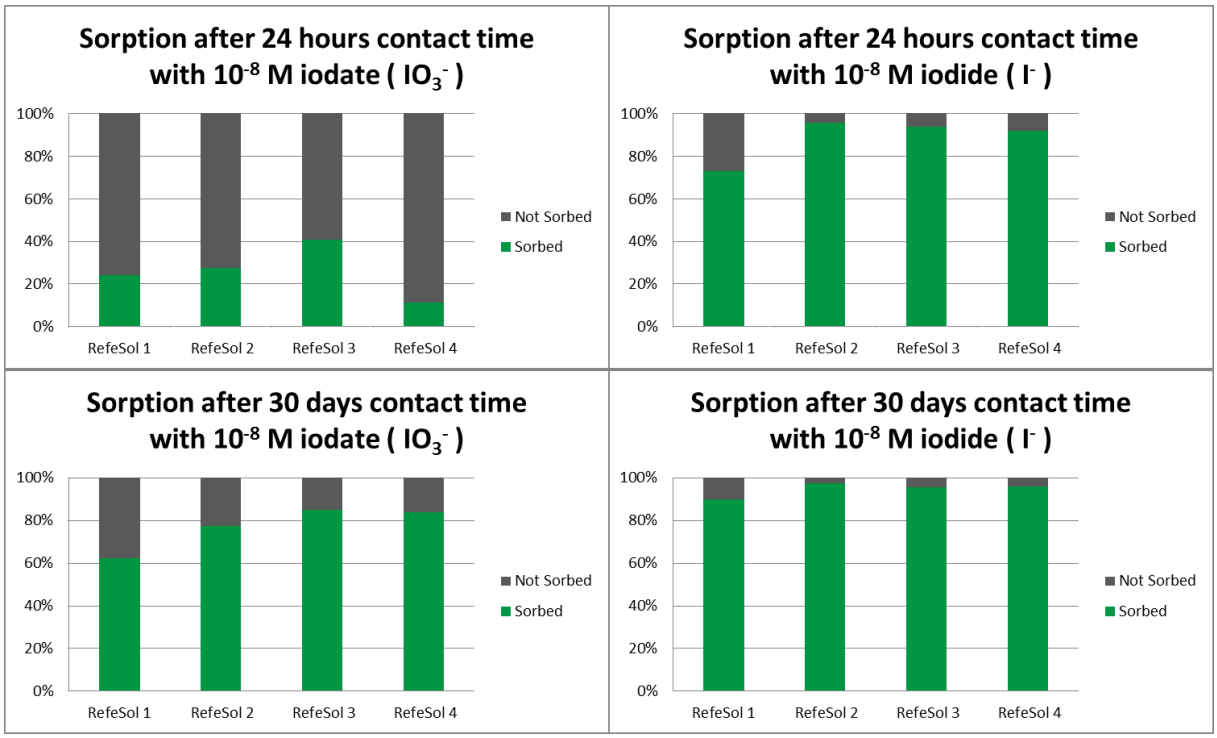

Figure 1: Sorption of iodate (left) and iodide (right) after a contact time of 24 hours and 30 days, respectively.

3.2 Iodide extraction

The results of the sequential extraction of iodide and iodate are given in (Fig. 2) and (Fig. 3). Calculated percentages represent the amount of iodine found in different fractions divided by total iodine adsorbed to soil. Residual iodine in soil after the sequential extraction is considered to be insoluble.

After 30 days of continuous contact with iodide solution two effects can be seen: The total amount of iodide adsorbed increased for all soils, whereas the amount of iodide found in the readily soluble fraction (water soluble and exchangeable fraction) decreases. As a result of longer contact time, iodide is bound stronger to the soil matrix, and more iodide can be found in the organic matter and metal oxide fractions at cost of iodide in the aforementioned fractions. This result indicates rearrangement processes taking place after the initial binding reaction, leading to stronger bound organo-iodine species.

For all four reference soils similar fraction patterns could be identified. In the first extraction step ultra-pure water was used to remove unbound iodide that remained in soil pore water. Only small amounts of iodide could be found in the water soluble fraction and it appears that sorption of iodine added as iodide is almost complete as less than 4 % iodide was retrieved by leaching with water. RefeSol 3 and 4 (with high C_{org} content) show even lower values for the water soluble fraction as compared to RefeSol 1 and 2. This result confirms the overall understanding of rapid iodide sorption in soils with high SOM content.

In the second extraction step a buffer system consisting of ammonium acetate (NH_4Ac) was employed, retrieving iodide bound by electrostatic interaction, for example ionic bonding. Iodide found in this fraction is less than 9 % for all analyzed soils. RefeSol 1 shows the highest amount, while RefeSol 3 exhibits the least amount of iodide found in this fraction. This result is in line with the first fraction (water soluble iodide) and proves that strong binding processes take place quickly (within hours) after adding the iodine. Except for RefeSol 1, the total combined amount of leached iodide from the first two extraction steps appears to be less than 10 %. The third step, using NaOH to extract SOM, proves to be the most efficient step to retrieve iodide from soil. For RefeSol 2, 3, and 4 the measurement yielded 84, 83, and 80 %, respectively. RefeSol 1 differs from the other soils with an amount of 61 % iodide extracted. Nevertheless, this result is in line with sequential extraction results from other studies (Englund et al., 2010; Luo et al., 2013). Iodide added to soil is bound to SOM within a short time period, indicating a fast reaction with soil organic matter. Recent studies (Bowley et al., 2016; Shetaya et al., 2012) suggest the formation of intermediates further reacting in an electrophilic substitution reaction with aromatic binding sites as can be found for example in humic substances as the most probable reaction process. However, the intermediate step proves difficult as neither the products nor exact time scales could be identified yet. Formation of hypoiodous acid (HIO) or elemental iodine (I_2) after oxidation of iodide is a common theory, even though these products are very short lived due to dissociation processes.

In the last extraction step hydroxylamine hydrochloride is used as leaching solution for metal oxide phases. Less than 2 % of the iodide added could be retrieved which indicates weak sorption of iodide to metal oxides in soil.

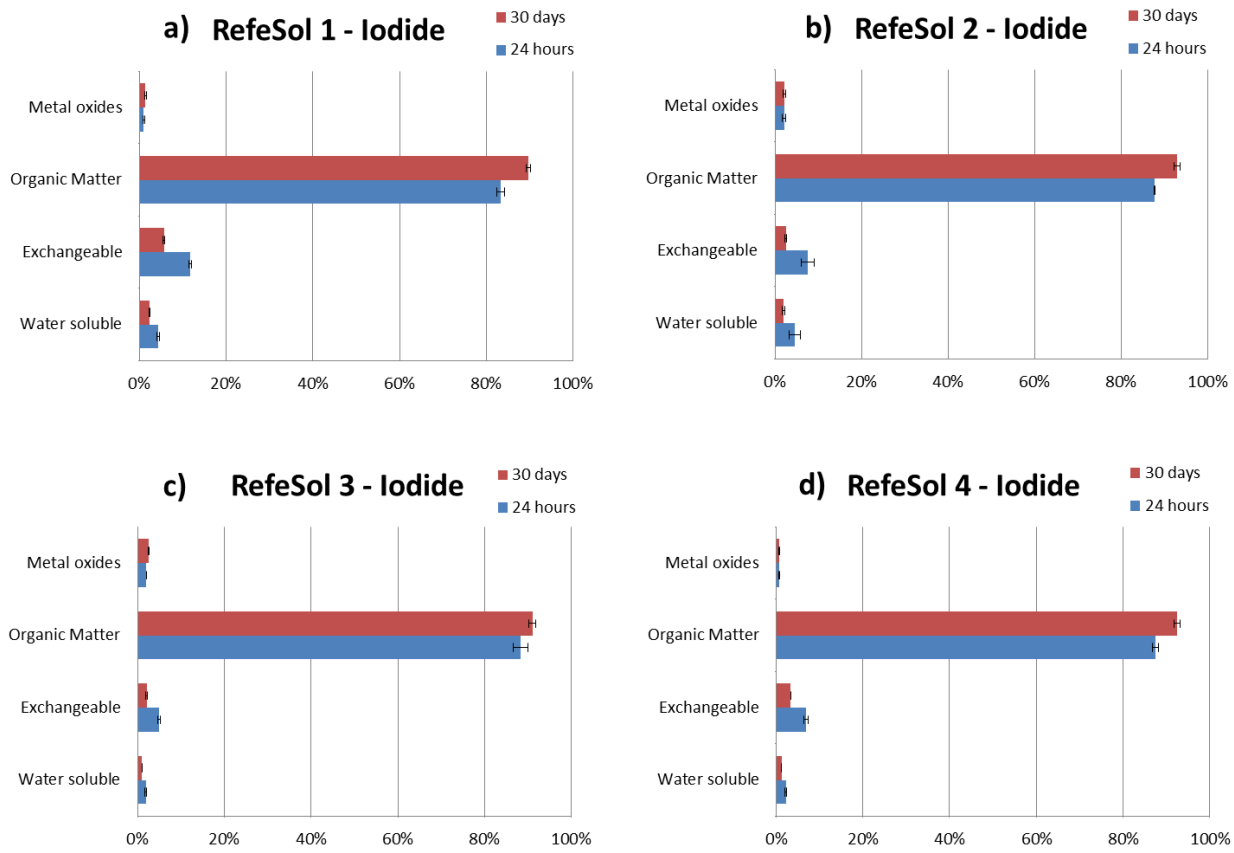

Figure 2: Distribution (%) of iodide adsorbed in German reference soils after a contact time of 24 hours and 30 days, respectively.

3.3 Iodate extraction

Analogous extraction experiment as described in the previous paragraph for iodide were performed for iodate sorption: After a contact time of 24 hours, considerable amounts of adsorbed iodate are released when using deionized water or a buffer solution for extraction. 30 – 48 % are found in the water-soluble fraction; 12 – 20 % are removed by buffer solution. The readily desorbable iodate accounting for 42 – 68 % after a contact time of 24 hours can be considered mobile. However, for RefeSol 3 and 4 iodate in amounts as high as 64 % and 41 %, respectively, are found in the organic fraction due to higher content of organic matter. The low sorption capacity and the distinct extraction pattern indicate weak bonding and slow reaction mechanisms. Compared to iodide the iodate interaction is weak for every analyzed soil.

After long time contamination of soil, iodate extraction pattern develop towards the ones measured for iodide. After 30 days contact time the amount of adsorbed iodate increases by

a factor 2 – 7 for different soil types, allowing for the correlation of iodate sorption and soil characteristics to become more apparent. Increased contact time reduces solubility in water and buffer solution from 38 to less than 5 % for RefeSol 4 and from 67 % to less than 20 % for RefeSol 1. Instead, more than 75 % of iodate adsorbed for RefeSol 1 and more than 80 % for the other RefeSol soils are found in the organic fraction. Except for minor differences, the extraction pattern of iodate after 30 days resembles the iodide extraction pattern after 1 day of contact time.

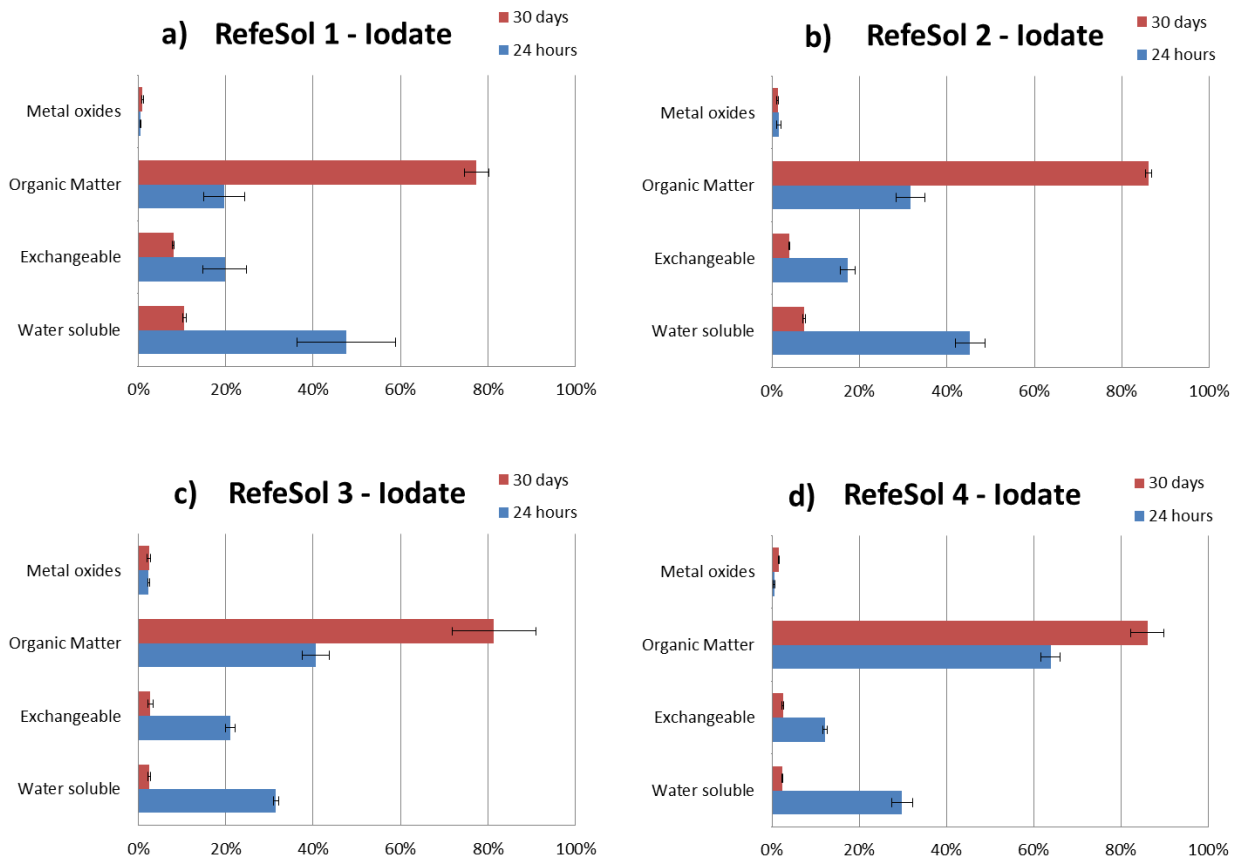

Figure 3: Distribution (%) of iodate adsorbed in German reference soils after contact time of 24 hours and 30 days contact time, respectively.

3.4 X-ray absorption spectroscopy

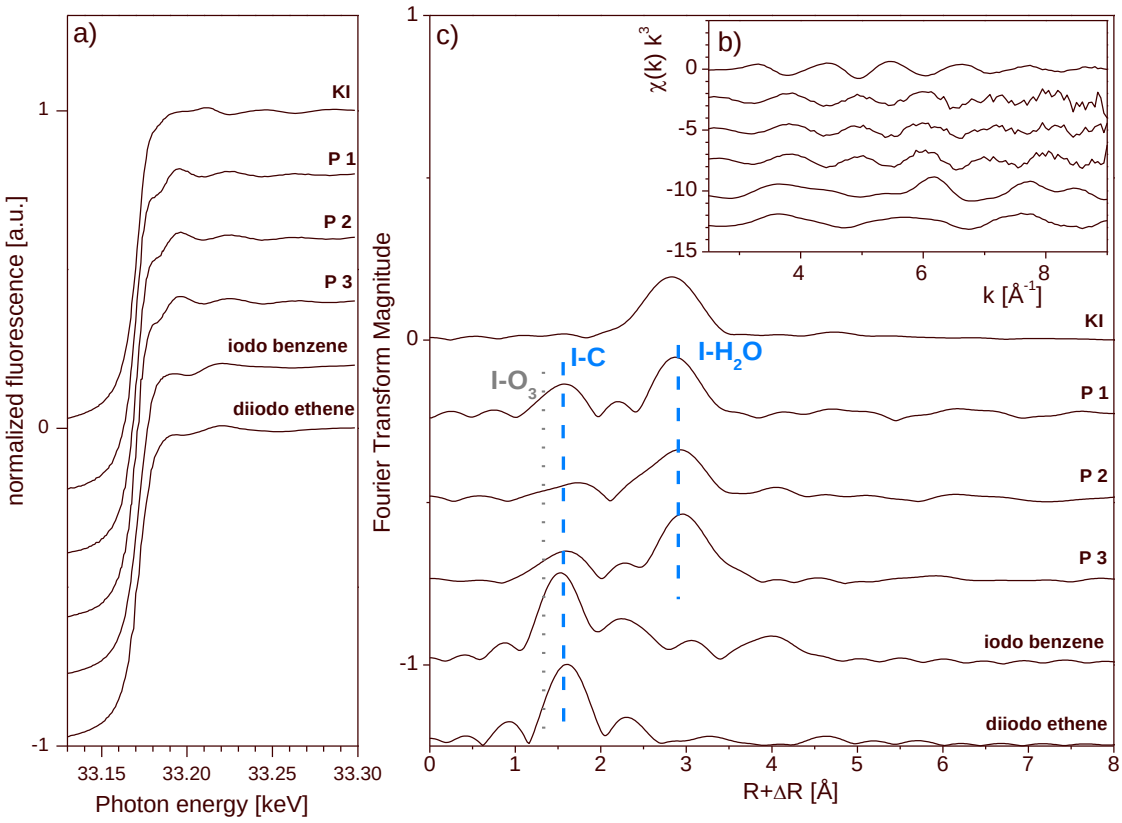

Figure 4: Iodine K-edge XAFS spectra of iodide-sorbed soil samples. a) XANES, b) k3-weighted chi spectra and c) corresponding Fourier Transform magnitude.

As expected from the -1 oxidation state, the XANES of iodide (Fig. 4a) is rather featureless without stronger electronic structure, and therefore shows only EXAFS features, i.e. interference patterns arising from the interaction of the outgoing photoelectron wave with neighboring atoms. The small spectral changes between KI, the three soil samples and the iodo-benzene reference are due to their different short range structure, while they do not show changes in oxidation state. Especially existence of iodate can be fully excluded, since its strong white line would be visible even at low iodine fraction (<1-2%, see Fig. 5a). Note that the edge energy, determined as the inflexion point of the raising XANES edge, is similar for all samples including those with pentavalent I (given its large error due to the large core hole lifetime widening of approx.10 eV), hence cannot be used to distinguish the two iodine oxidation states.

The Fourier Transform Magnitudes (FTM) representing a pseudo radial distribution function around I („pseudo“, since the radial distances are not corrected for phase shift) of KI and the three soil samples are dominated by a peak at about 2.8 Å (Fig. 4c). For KI, this arises from backscattering of a nearest shell of K atoms. The shell fit provides 5.3 K atoms at 3.45 Å, hence shorter than the 3.52 Å determined by other methods (Cortona, 1992). This difference may arise form a partial hydration of the KI powder used for EXAFS analysis, since the hydration sphere of hydrated iodide in the soil samples appears at almost the same FTM position as that of K in KI. A shell fit of this peak results in 5 to 6 O atoms at 3.54 to 3.56 Å, in

line with the local structure of the iodide anion in water determined earlier also by I K-edge EXAFS spectroscopy (Tanida and Watanabe, 2000).

Besides this FTM peak at 2.8 Å, however, there is also one at a lower distance of about 1.6 Å. This peak is at a slightly longer position than that of IO3 (shown as a gray hatched line in Fig. 4c), but agrees well with the I-C path of organo-iodine compounds. In case of aromatic-bound I, this path should have a distance of 1.99 to 2.07 Å, while it is slightly, but significantly longer for aliphatic-bound I (2.15 to 2.16 Å) (Schlegel et al., 2006). This is also confirmed for our two organo-iodine references, where shell fit provided a I-C path of 2.09 Å in length for iodo-benzene, and 2.16 Å for diiodo-ethane (Table 3). When fitting this I-C path to the soil samples, distances of 2.10 to 2.13 are provided, which are slightly larger than those expected for I bound to aromatic groups, but significantly shorter than those expected for I bound to aliphatic groups (Table 1). The coordination numbers of 0.3 to 0.4 (nominally 1) suggest that 30 to 40% of iodine is bound to organic groups, while the remainder would prevail in the iodide anion form; it should be noted, however, that the error in coordination numbers is large (typically ± 30 %), hence the quantitative speciation based on EXAFS-derived coordination numbers also has a large error. It can be concluded, however, that two iodine species occur in all three soils samples treated with iodide, i.e. as iodide anion and the organo-iodine, most likely bound to aromatic groups.

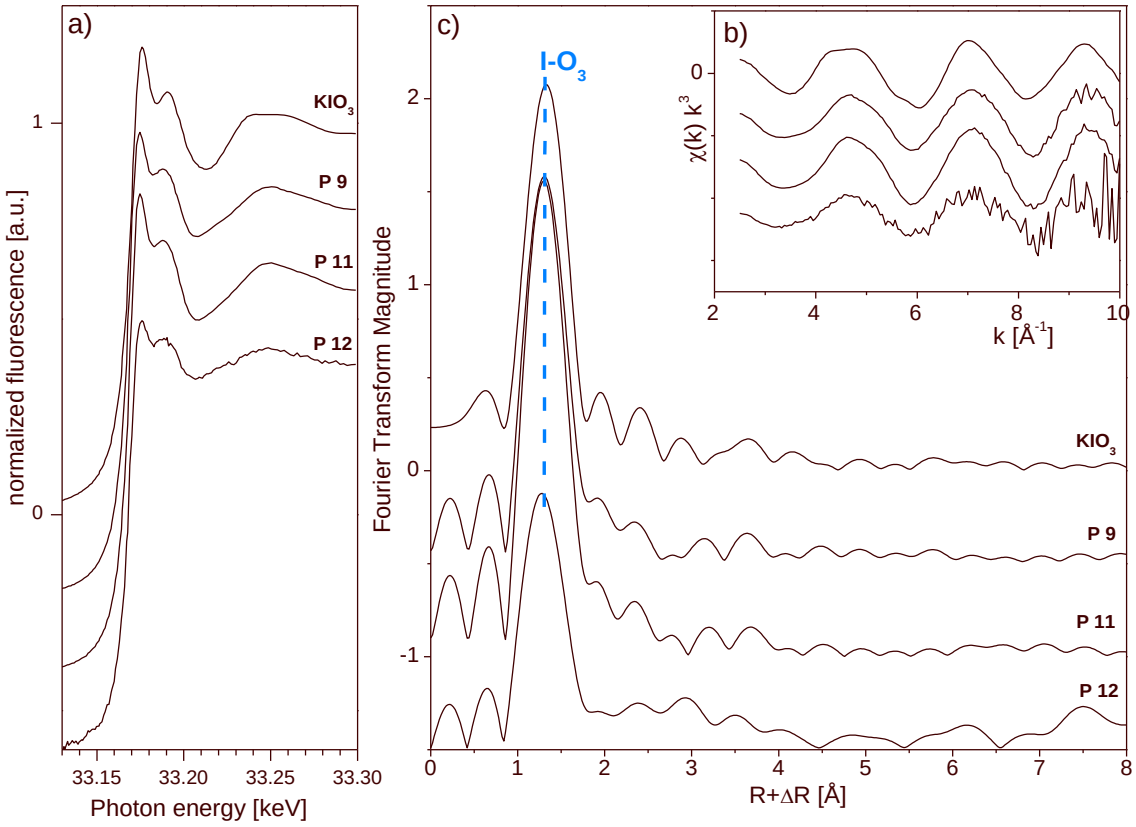

Figure 5: Iodine K-edge XAFS spectra of iodate-sorbed soil samples. a) XANES, b) k3-weighted chi spectra and c) corresponding Fourier Transform magnitude.

The XANES spectra of the pentavalent iodate KIO_3 (Fig. 5a) show a double white line peak, where the first one can be assigned to the transition of the ejected 1s electron into the free valence orbitals (1s ~ 4p quadrupole transition), while the second one is due to multiple scattering within the IO_3 unit. The XANES spectra of the iodate-treated soil samples are very similar, suggesting that the pentavalent oxidation state of I was conserved in these samples.
The short range structure of KIO_3 is dominated by a strong peak of the Fourier transform magnitude (FTM) at about 1.4 Å, which should arise from the three oxygen atoms of the IO_3 unit. This is confirmed by the shell fit, providing 3.1 O atoms at 1.80 Å (Table 4). This local structure is maintained for the three soil samples (Fig. 5 and Table 4). Note that the coordination number of only 2.1 for sample P12 may be an effect of the relatively high noise level of the EXAFS spectrum of this dilute sample. The FTM of all soil samples shows only noise beyond this coordination shell, hence there is no indication for the formation of inner sphere sorption complexes. This does not allow us to exclude the formation of such complexes, since they may be invisible due to the large static disorder expected for such pyramidal oxyanions (note that the EXAFS measurement at about 12 K precludes thermal (vibrational) disorder).

Table 4: XAFS edge energies (E) and shell fit parameters (S02=0.9).

Sample	E	Coordination shell			Further shells			ΔE_0 [eV]	χ^2_{res} %
	[eV]	CN	R [Å]	σ^2 [Å^2]	CN	R [Å]	σ^2 [Å^2]		
KI	33,169.4	5.3 K	3.45	0.0233				1.1	3.1
P1	33,170.4	0.3 C	2.11	0.0010	5.3 O	3.54	0.0079	8.4	8.2
P2	33,171.0	0.4 C	2.13	0.0010	5.8 O	3.54	0.0100	8.2	12.2
P3	33,170.6	0.4 C	2.10	0.0010	5.1 O	3.56	0.0062	9.5	11.9
Iodo benzene	33,171.7	1.1 C	2.09	0.0014	2 C 4 MS	3.01 3.25	0.0037 0.0010	7.5	8.7
Diiodo ethane	33,171.5	1.2 C	2.16	0.0039				6.9	6.0
KIO_3	33,170.2	3.1 O	1.80	0.0009				15.8	4.9
P9	33,169.0	3.0 O	1.80	0.0005				15.3	8.0
P11	33,168.9	3.3 O	1.79	0.0005				15.5	12.8
P12	33,169.0	(2.1 O)	1.79	0.0013				12.6	14.4

4. Discussion

A clear distinction between the iodine species can be observed, especially with regard to reaction time and extent of iodine adsorption. After a contact time of 24 hours the amount of adsorbed iodide is as high as 70 – 90 % of added iodide being located in the solid phase. Variations regarding the amount of adsorbed iodide can be explained with the different soil types used. In contrast, iodate adsorbed was less than 20% for all soil types under the same conditions. Iodate adsorption increases to amounts of 63 – 85 % after a contact period of 30 days, indicating different, slower reaction pathways.

The ability of iodide to form chemical bonding to soil organic matter (SOM) allows for a fast reaction pathway for sorption processes when organic substance is available. The electrophilic substitution mechanism might lead to direct binding after a short period of time, due to binding sites being present in SOM. This has been stated for the iodination of humic acids and proves to be the dominant reaction directly after addition of iodide (Reiller and Moulin, 2003; Schlegel et al., 2006). Further increase of iodide sorption most likely is the result of different reaction pathways. As pH and Eh in soil vary, the most probable assumption is oxidation of iodide to different, intermediate species such as water soluble molecular iodine ($I_{2(aq)}$), hypoiodous acid (HIO), or triiodide (I_3^-) (Reiller and Moulin, 2003). Transformation into different species allows for more reaction pathways, like electrophilic substitution of phenolic, carbonyl or methyl compounds (Schlegel et al., 2006).

In contrast, iodate does not perform electrophilic substitution at available binding sites of SOM as main reaction pathway. Electrostatic interaction with metal oxide phases is described as first step binding mechanisms for iodate (Dai et al., 2004). Strength of electrostatic bonding is weaker than covalent bonding, and therefore provides relatively weak sorption. However, in closed batch experiments long time reactions are influenced by changing redox conditions due to microbial activity resulting in oxygen depletion. For instance, reduction processes can be introduced by denitrifying bacteria or abiotically by compounds containing functional groups such as lignin or tannin (Kaplan et al., 2014; Zhang et al., 2014). Iodate having an oxidation state of +5 is reduced at a redox potential of 0.7 – 0.8 V as a function of the pH-range of 5.2 to 6.6 established for the RefeSol soils we analyzed. No external oxygen supply was included, and thus reduction of iodate to iodide is very likely to occur. Increased binding to SOM due to change in iodine species takes place. Therefore, similar sorption capacity and extraction pattern for iodide (24 hours) and iodate (30 days) might be a result of this change in species. Migration of iodate is most probable during first days and weeks after input, until reduction processes sets in. A fast reaction step leading to initial retardation of iodine in soil is electrostatic bonding on metal oxides. However, the main reaction resulting in immobilization of both iodine species in soil probably is the reaction with SOM followed by forming of covalent bonding after electrophilic substitution.

XAS results prove the high reactivity of iodide with SOM, leading to transformation of inorganic to organically bound iodine after short contact times. Signals of investigated soil samples agree well with I-C bond length of investigated reference substance (iodo-benzene),

which indicates that the main binding site for iodide should be aromatic compounds within the SOM. This confirms the results of other studies (Schlegel et al., 2006), even though calculated coordination numbers depict both organo-iodine and iodide anion in solution. Partial hydration is the most probable reason for shorter radial distances, which were found in KI reference samples as well as analyzed soil samples.

For addition of iodate to soil, XAS spectra should show the formation of organo iodine; yet, no change in speciation can be observed even after long-term contact. As stated before, formation of inner sphere sorption complexes cannot be excluded due to large static disorders, which occur for oxyanions. However, constant iodate signals in each soil after different treatments point towards secondary reaction pathways, which for iodate only take place after longer contact times (more than 30 days). Sterilization of soil as well as air drying showed little influence on FTM bond length for iodate.

It is stated that oxygen ventilation results in iodate being the predominant chemical species, which represents possible environmental conditions (Hansen et al., 2011). However, anoxic conditions lead to a reduction of iodate to iodide, which most likely happened during this work using closed vials in the batch experiments. Aerated soil systems provide increased migration potential for iodate and therefore a possible pathway to the human. Conclusively, for evaluation of risk potential of iodine releases into the environment, contamination pathways and species have to be considered for natural circumstances. High sorption of iodide to organic matter provides retardation potential in the top layers of soil. However, for iodate risk of further spreading is higher due to its slow sorption. The next stage in this field of study comprises column experiments with RefeSol soils to counter disadvantages of batch experiments. Thereby, change in species, sorption capacities and iodine-soil interactions by capillary ground water, respectively, can be determined more accurately for natural soil systems.

According to the results of this study, metal oxides do not provide important sorption sites for iodate. This finding is in contradiction to results of sequential extractions performed in other studies (Hansen et al., 2011). A correlation between iron and aluminum oxides, respectively, and iodate sorption was described (Dai et al., 2009; Dai et al., 2004). The reason for this deviation is most probably due to the fact that we used uncontaminated soil samples in our study, introducing ‘fresh’ iodine. Natural soil samples comprise longer contact time with long-lived radioiodine (^{129}I), at least years up to decades. By contrast, reaction pathways after short time contact are described in this study. Considering the reaction of iodate in soil as two-step mechanism gives an explanation for small sorption as first step followed by a slower step that results in formation of stronger bonding to metal oxides (Nishimaki et al., 1994) and SOM.

This study broadens the knowledge about the time dependent sorption behavior of iodine in German reference soil, especially for risk evaluation after possible leakage scenarios. Little sorption is given for both investigated iodine species for concentrations higher than 10^{-8} M. Contamination of ground water in combination with capillary rise is most likely to contribute to iodine migration into the biosphere and, subsequently, to the food chain. Further studies should focus on these transfer pathways, which have to be considered critical for iodine.

5. Conclusions

This study demonstrates that sorption of iodine in soil shows a dependency on the species in which the element is present. The experimental setup was kept constant as iodide and iodate were added to different German soils in batch experiments. Yet, results prove distinct differences between the species regarding sorption behavior. Furthermore, the different soil types prove to influence iodine sorption. The amount of adsorbed iodine is higher for iodide than for iodate as direct iodination of soil organic matter (SOM) is only possible for iodide. By contrast, added iodate revealed only weak interaction with soil after 24 hours contact time, followed by a slow adsorption and primary reaction. Determination of species after addition of iodate confirmed the assumption of longer time scales necessary for sorption of the pentavalent iodine species in soil. Desorption of iodate was facilitated by adding weak extraction solutions like deionized water and buffer solution, respectively. Long time contamination of soil systems allows for different reaction mechanism, such as oxidation and reduction of involved analytes. Intermediate stages develop and secondary reaction pathways become possible. Final reaction steps lead to iodinated organic molecules for iodide. XAS measurements prove formation of organo-iodine compounds for addition of iodide after short contact time. Bond length indicates aromatic-bound iodine rather than iodine bound to aliphatic groups. When bound to soil, iodine appears to be insoluble for deionized water and buffer solutions. Thus, mobility of iodine in organic rich soils is relatively low. However, this statement loses validity when high amounts of iodide are added as sorption capacity for iodine is low for the analyzed German reference soils. The risk of transport to the biosphere is given, when high amounts of iodine are released to groundwater, whereas iodine in trace concentrations, as expected leaking from a nuclear waste repository, is most likely effectively immobilized or at least strongly retarded. When contamination of top soil with high amounts of iodine occurs, migration into deeper layers is most likely to take place. Furthermore, co-transport via dissolved organic matter has to be taken into account, as well as the influence of microbial activity on iodine sorption, which is not fully understood. Batch experiments are an effective way to determine sorption capacities; however, batch experiments are not the method of choice for migration prediction. Conclusively, for more detailed prediction for iodine migration in soil after release during a nuclear accident or from a nuclear waste repository, further studies are necessary.

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Table 1

Table 1: Soil characteristics as analyzed by Fraunhofer Institute for Molecular Biology and Applied Ecology (IME), and iodine content in mg kg^{-1} (=ppm) by ICP-MS.

	sand [%]	silt [%]	clay [%]	pH ($CaCl_2$)	C_{org} [%]	N [g/kg]	CEC_{eff} [mmol kg^{-1}]	Iodine content [ppm]
RefeSol 1	76.7	17.2	6.10	5.33	0.80	0.71	17.9	0.69
RefeSol 2	2.30	82.0	15.7	6.63	0.98	1.25	53.4	0.84
RefeSol 3	17.7	57.5	24.8	5.91	3.05	3.57	73.5	1.81
RefeSol 4	82.7	12.7	4.60	5.22	2.79	1.41	37.3	0.79

Table 2

Table 1: Sequential extraction procedure with used chemicals and parameters.

Extraction steps	Extracting agent	Temperature (°C)	Contact time (hours)	pH	Dissolved fraction
Step 1	H_2O (dest.)	RT	2	soil	water soluble iodine
Step 2	1 M NH_4Ac	RT	2	7	exchangeable iodine
Step 3	0.3 M NaOH	80	6	14	iodine bound to organic
Step 4	0.04 M $NH_2OH*HCl$	80	6	3	iodine bound to metal(-oxides)

Table 3

Table 1: Prepared samples for XAS-measurements, contamination time and further treatment of soils.

Sample No.	Contact time [d]	Iodine species	Additional experimental conditions
P1	1	KI	---
P2	5	KI	---
P3	20	KI	---
P9	20	KIO_3	---
P11	20	KIO_3	Sterilization process
P12	20	KIO_3	Air dried after contamination

Table 4

Table 1: XAFS edge energies (E) and shell fit parameters (S02=0.9).

Sample	E	Coordination shell			Further shells			ΔE_0 [eV]	χ^2_{res} %
	[eV]	CN	R [Å]	σ^2 [Å^2]	CN	R [Å]	σ^2 [Å^2]		
KI	33,169.4	5.3 K	3.45	0.0233				1.1	3.1
P1	33,170.4	0.3 C	2.11	0.0010	5.3 O	3.54	0.0079	8.4	8.2
P2	33,171.0	0.4 C	2.13	0.0010	5.8 O	3.54	0.0100	8.2	12.2
P3	33,170.6	0.4 C	2.10	0.0010	5.1 O	3.56	0.0062	9.5	11.9
Iodo benzene	33,171.7	1.1 C	2.09	0.0014	2 C 4 MS	3.01 3.25	0.0037 0.0010	7.5	8.7
Diiodo ethane	33,171.5	1.2 C	2.16	0.0039				6.9	6.0
KIO_3	33,170.2	3.1 O	1.80	0.0009				15.8	4.9
P9	33,169.0	3.0 O	1.80	0.0005				15.3	8.0
P11	33,168.9	3.3 O	1.79	0.0005				15.5	12.8
P12	33,169.0	(2.1 O)	1.79	0.0013				12.6	14.4

Figure 1

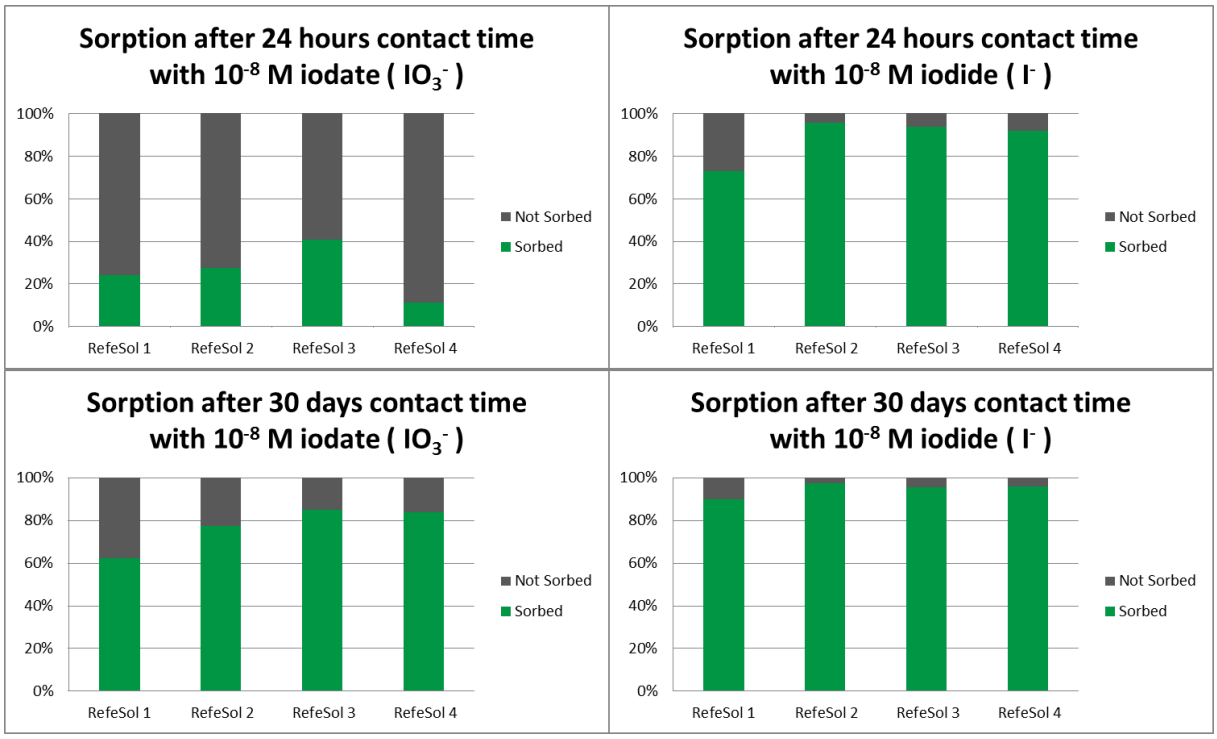

Figure 1: Sorption of iodate (left) and iodide (right) after a contact time of 24 hours and 30 days, respectively.

Figure 2

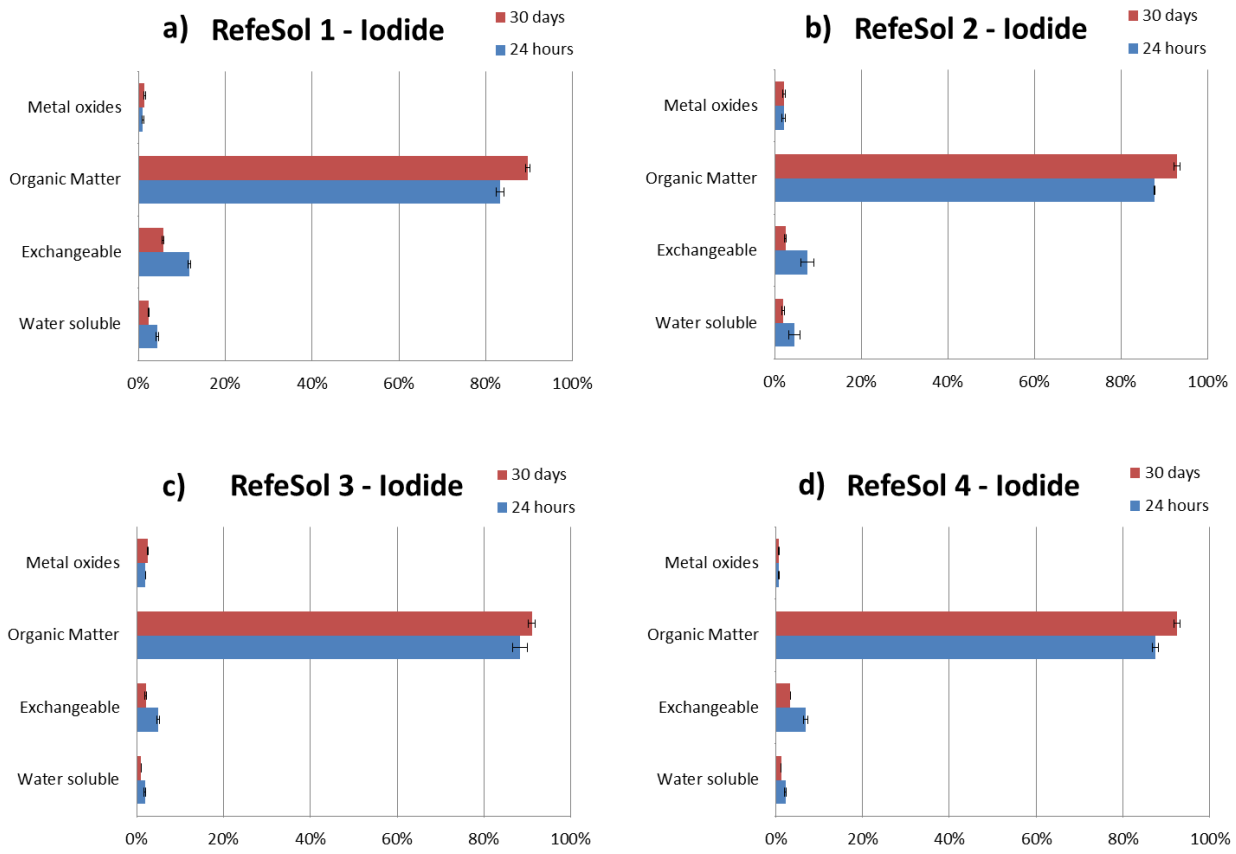

Figure 1: Distribution (%) of iodide adsorbed in German reference soils after a contact time of 24 hours and 30 days, respectively.

Figure 3

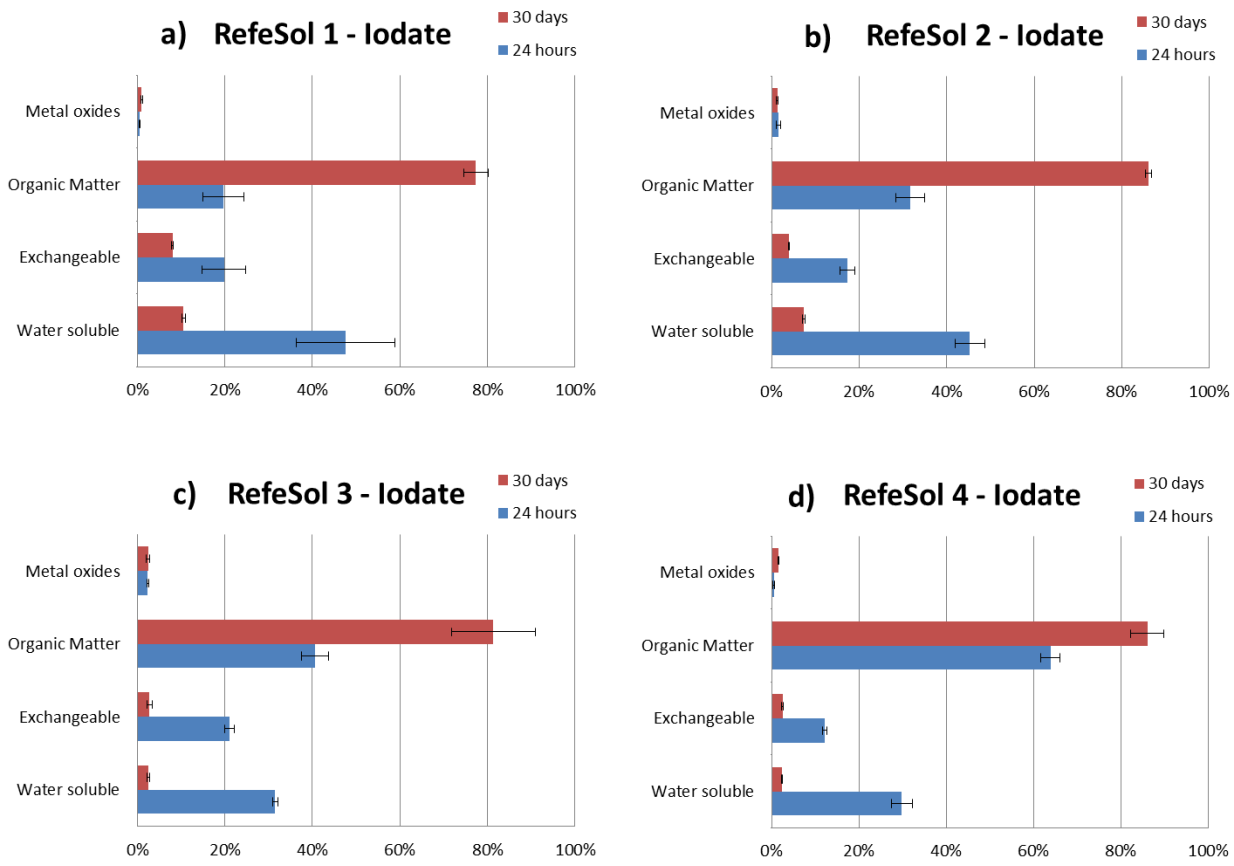

Figure 1: Distribution (%) of iodate adsorbed in German reference soils after contact time of 24 hours and 30 days contact time, respectively.

Figure 4

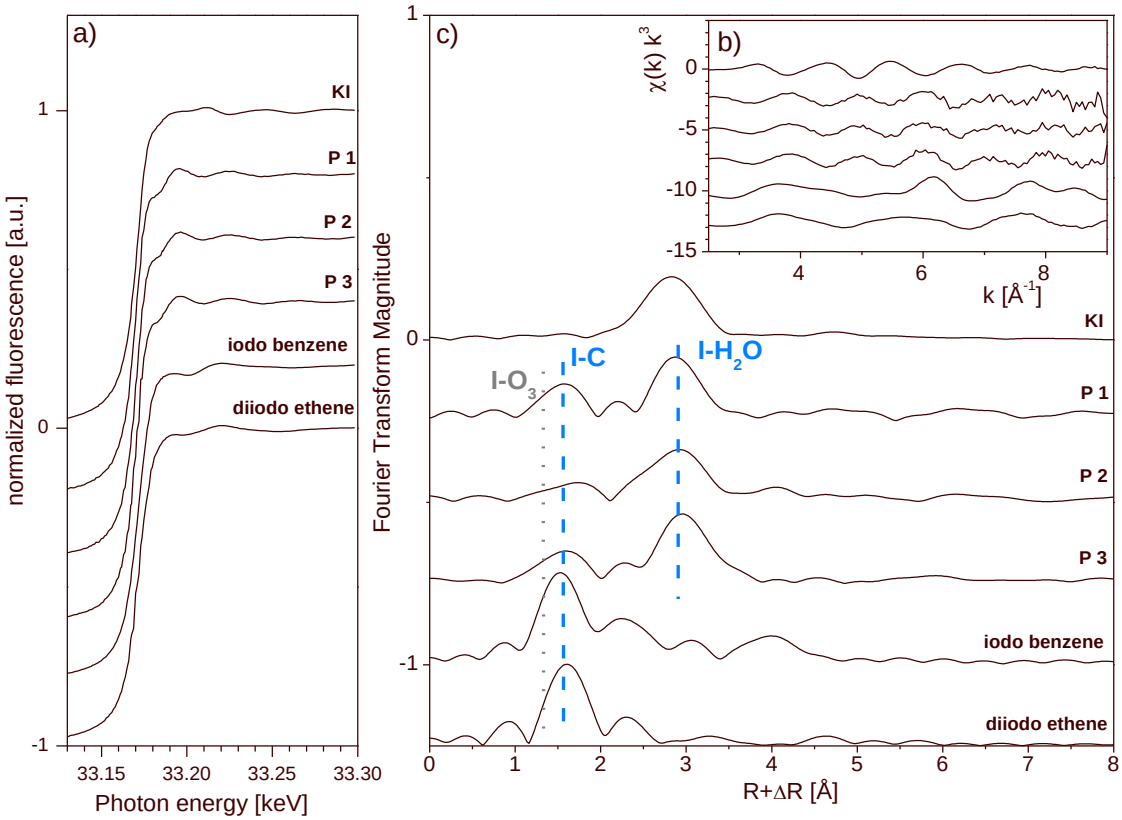

Figure 1: Iodine K-edge XAFS spectra of iodide-sorbed soil samples. a) XANES, b) k3-weighted chi spectra and c) corresponding Fourier Transform magnitude.

Figure 5

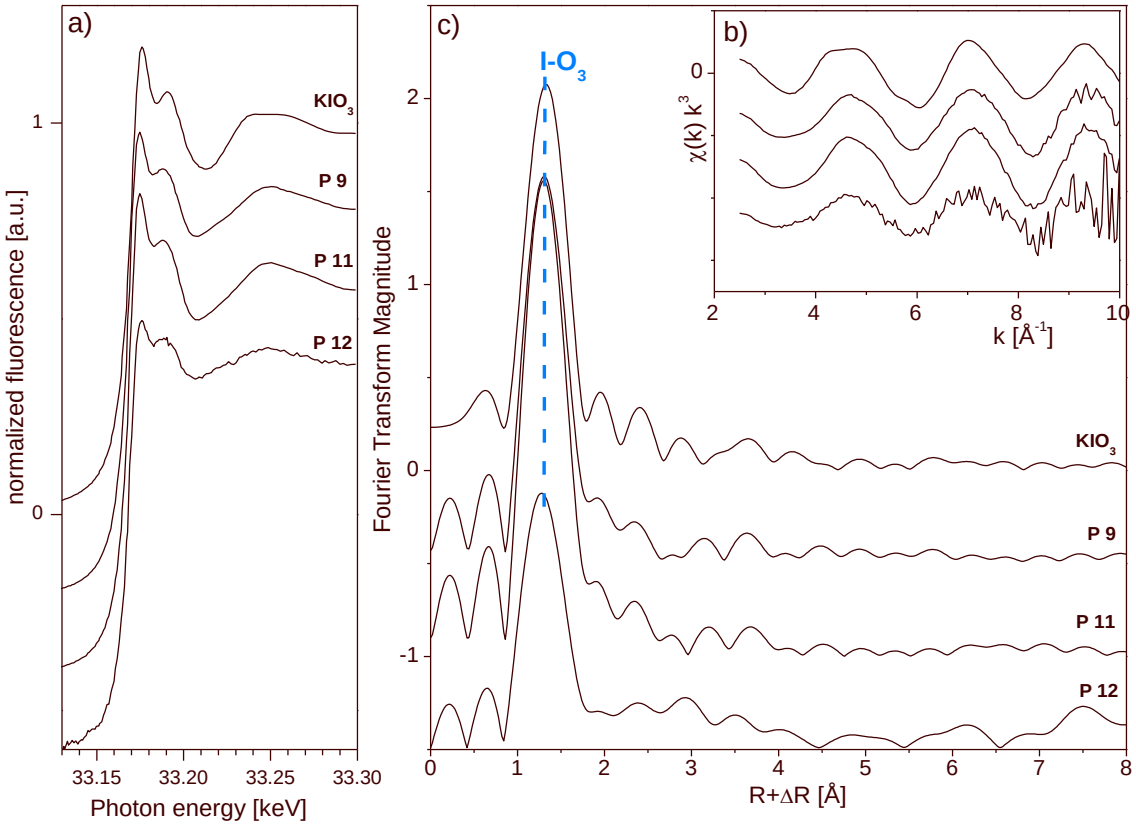

Figure 1: Iodine K-edge XAFS spectra of iodate-sorbed soil samples. a) XANES, b) k3-weighted chi spectra and c) corresponding Fourier Transform magnitude.