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SORPTION AND SPECIATION OF RADIONUCLIDES IN BOREAL FOREST SOIL

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To

My loved ones Emmi, Kaisla and Hannu

"Live long and prosper"
-Leonard Nimoy

ABSTRACT

In biosphere safety assessment of spent nuclear fuel, the importance of radionuclides increases with their possibility to induce radiation dose for humans and other organisms in the future. The surface environment migration and sorption of ^{135}Cs, ^{129}I, ^{93m,94}Nb and ^{79}Se is of great importance since these radionuclides have been assessed to contribute to the potential radiation dose in the most realistic biosphere calculation cases. This doctoral thesis aimed to investigate the retention and behaviour of cesium (Cs^+), iodine (I^- and IO_3^-), niobium ($Nb(OH)_5$) and selenium (SeO_3^{2-} and SeO_4^{2-}) in humus and rather undeveloped mineral soil of boreal forest on Olkiluoto Island when abiotic factors affecting the sorption reactions were varied. Factors affecting species transformations of iodine and selenium were also examined for the same soil samples and under the same experimental conditions.

Cesium retention was affected by e.g. incubation conditions, soil depth, pH, humus and mineralogy. Humus exhibited lower sorption of cesium than mineral soil, which was caused by mineral soil's relatively high muscovite content and the presence of Cs–selective FES sites in muscovite interlayer spaces. Formation of slightly reducing soil conditions decreased soil retention of cesium, presumably caused by the formation of NH_4^+ ions and arisen competition of the FES sites. Increase in soil pH accelerated the retention of cesium on negatively charged surface sorption sites.

The highest retention of inorganic iodine forms iodide and iodate were observed in humus, as caused by sorption processes and speciation changes leading to presumable formation of organo–iodine compounds in microbially mediated reactions. Iodine sorption on mineral soil was very low in aerobic and anaerobic soil conditions, even though acidic pH values increased the retention. Decrease in pH had similar effect for selenium (selenite) and niobium. For these two elements inorganic soil components, and especially weakly crystalline aluminium and iron oxides are considered important retentive phases due to inner sphere complexation with surface Al and Fe atoms.

Speciation of iodine showed considerable dependence on soil environment. Iodate was reduced to iodide especially in anaerobic soil conditions, low pH and in the presence of organic matter and microbial activity. No oxidation of iodide to iodate was detected. Formation of unidentified, presumable organo–iodine compounds was observed in humus and mineral soil of low pH or varying incubation time. Inorganic selenium forms selenite and selenate proved to be persistent in the experimental conditions as no changes in selenium liquid phase speciation was observed irrespective of variation in incubation time, pH or redox potential.

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Hey you all, we finally did it!

Espoo, September 2016

Mervi Söderlund

CONTENTS

LIST OF ORIGINAL PUBLICATIONS

This thesis is based on the following publications, which are referred in the text by their Roman numerals (I – V):

I   M. Söderlund, M. Hakanen, J. Lehto: Sorption of niobium on boreal forest soil. *Radiochimica Acta* **2015**, 103 (12), 859-869

II   M. Söderlund, M. Hakanen, J. Lehto: Sorption of cesium on boreal forest soil I: the effect of grain size, organic matter and mineralogy. *Journal of Radioanalytical and Nuclear Chemistry* **2016**, 309(2), 637-645

III   M. Söderlund, S. Virtanen, I. Välimaa, J. Lempinen, M. Hakanen, J. Lehto: Sorption of cesium on boreal forest soil II. The effect of time, incubation conditions, pH and competing cations. *Journal of Radioanalytical and Nuclear Chemistry* **2016**, 309(2), 647-657

IV   M. Söderlund, J. Virkanen, S. Holgersson, J. Lehto: Sorption and speciation of selenium in boreal forest soil. *Journal of Environmental Radioactivity* **2016**, 164, 220-213

V   M. Söderlund, J. Virkanen, H. Aromaa, N. Gracheva, J. Lehto: Sorption and speciation of iodine in boreal forest soil. *Journal of Radioanalytical and Nuclear chemistry* **2016**, DOI: 10.1007/s10967-016-5022-z

Author's contribution to the publications I – V:

The author planned all the experimental work for publications I – V. The execution of the experimental work for Manuscripts I, II, IV and V was performed solely by the author and for publication III together with part of the co-authors. The specific surface area analysis of mineral soil and individual minerals in publication IV was done by S. Holgersson at Chalmers Technical University in Gothenburg, and the respective analyses for Manuscripts I and II were performed at Tampere Technical University. The XRD analyses of the mineral soil samples in Manuscript I were carried out at the Geological Survey of Finland, Espoo. All Manuscripts were written by the author.

ABBREVIATIONS

BSA   biosphere safety assessment
CEC   cation exchange capacity
CO_2 carbon dioxide
DOC   dissolved organic carbon
DW   dry weight
FES   frayed edge sites
GTK   Geological Survey of Finland
HCl   hydrochloric acid
HIO   hypoiodous acid
HPLC–ICP-MS high performance liquid chromatography combined with inductively coupled plasma mass spectrometry
I_2 molecular iodine
IRF   instant release fraction
K_d (mass) distribution coefficient
Kr–BET   Kr gas adsorption Brunauer-Emmett-Teller model
LMW   low molecular weight
LOD   analytical limit of detection
MSS   model soil solution
N_2–BET N_2 gas adsorption Brunauer-Emmett-Teller model
NaOH   natrium hydroxide
O_2 molecular oxygen
OM   organic matter
OM–I   organo–iodine
OM–Se   organo–selenium
PE   polyethylene
$p$$K_a$ logarithm of acid dissociation constant
$p$$K_b$ logarithm of base dissociation constant
PP   polypropylene
SNF   spent nuclear fuel
SOM   soil organic matter
STDEV   standard deviation
SSA   specific surface area
XRD   X-ray diffraction spectroscopy

1 INTRODUCTION

In the year 2015, 33.7 % of the consumed energy in Finland was produced in four operating nuclear power reactor units in Loviisa and Olkiluoto [1]. The production of nuclear energy creates highly radioactive spent nuclear fuel (SNF), which needs to be disposed safely ensuring that it does not or will not cause any radiation harm to human health or any other harm to environment or other property. The responsibility on the verification of these requirements rests on the shoulders of the party implementing the final disposal.

1.1 FINAL DISPOSAL CONCEPT OF SPENT NUCLEAR FUEL AND BIOSPHERE SAFETY ASSESSMENT

The final disposal of SNF is to be conducted in a deep underground repository in the granitic crystalline Olkiluoto bedrock at the depths of 400−450 m [2]. The disposal will be carried out without fuel reprocessing by SKB−3V method, which was originally developed in Sweden by Svensk Kärnbränslehantering AB. In this method, the SNF capsules are inserted vertically in individual deposition holes bored to the ground of the deposition tunnels [3]. The safety of SNF is planned to be achieved through long−term isolation and containment of SNF from biosphere and surface environment. This will ensure radioactivity to decay to acceptable levels, e.g. 100 000 years after the emplacement the radioactivity of SNF capsules has decayed to one 3000th part [4,5]. The isolation of SNF is achieved by safety barriers including UO_2 fuel matrix itself, copper canisters with cast iron inserts, bentonite buffer surrounding the canisters, tunnel backfill material and finally host bedrock as a natural barrier [3,4,6,7]. The properties of the safety barriers are such that very slow radionuclide release rates from the containments and dispersal within the geosphere can be achieved after the isolation of SNF has been ended due to water penetration into the final repository and mixing of radionuclides within the liquid phase [5]. The safety barriers are designed to work independently but support each other.

A common factor for the malfunctioning of the safety barriers is the diffusion of water either into the vicinity or through the barrier and consequently away from it. The action of bedrock as a natural barrier for SNF lies within its low hydraulic conductivity (i.e. slow water diffusion rate) [4,8]. In situations where radionuclides have escaped the repository, significant retardation in the bedrock can be expected due to radionuclide−mineral surface interactions and long distances to surface environment. Tunnel backfill material is engineered to slow water diffusion rate to at least the same, or preferably smaller water hydraulic conductivity level as met in the

surrounding intact bedrock [7]. When water reaches bentonite buffer, bentonite will swell caused by the diffusion of water molecules into the interlayer spaces of its main component montmorillonite mineral. In addition to swelling, bentonite is expected to limit the inwards transport of groundwater corrosive components (e.g. O_2, S^{2-}) to copper canisters by forming a chemically and mechanically protective layer [7]. Another function of bentonite buffer is to retard the outward release of mainly cationic radionuclides (e.g. Cs^+) by ion exchange reactions [9-12]. The copper canisters surrounding the SNF are expected to isolate SNF from its environment for approximately 100 000 years, a time limit that can vary depending on the possible canister malfunctions and corrosion intensity [13,14]. In addition to SNF, the copper canisters protects their cast iron inserts which give radiation shielding and mechanical strength for the canisters [7]. The operational idea of UO_2 fuel as the innermost safety barrier is based on its low solubility in the expected reducing repository conditions with low water supply [4,7]. Thus, the dissolution rate of UO_2 dictates the release rate of radionuclides mingled within the matrix [15]. Radionuclides included in the instant release fraction (IRF), such as noble gases and a fraction of cesium and iodine, are liberated immediately after water penetrates the copper canister interiors [7,15].

The long–term safety of SNF final disposal is evaluated in biosphere safety assessment (BSA) [3]. The objectives of BSA includes assessing the probabilistic Olkiluoto surface environment conditions and processes acting nowadays and in the future. However, the main target is on the evaluation of the probable radiological consequences caused to a man and other living beings followed by a hypothetical radionuclide release from the repository into the geosphere and further into the surface environment and distribution within. The likely radionuclide release points are linked to aquatic environments, such as lakes, but the release into terrestrial environments cannot be ruled out. In BSA, special importance is on radionuclides (^{14}C, [36]Cl, [129]I) which themselves or their progenies are expected to dominate the induced radiation dose in most of the (realistic) hypothetical biosphere releases [3]. As the contribution of radionuclides to the radiation dose decreases, their classification drops from top priority into high priority groups according to their relevance for SNF long–term safety.

This thesis work focuses on cesium, iodine, niobium and selenium. Each of these elements have radionuclides bearing significant importance in BSA most notably due to their long physical half–life and high inventory in SNF, and possibly also by their expected low retention/high migration caused by their chemical forms in the repository conditions and in the bedrock [3,16]. In BSA calculations the most important processes radionuclides are to experience are diffusion, sorption and solubility limited reactions [15]. The release of the radionuclides from UO_2 fuel matrix and other metallic parts are expected to be limited by the degradation rate of these components, whereas inside the copper canister, bentonite buffer and tunnel backfill material radionuclide solute concentration may be limited by radionuclide solubility [15]. Cesium and

iodine are expected to have unlimited solubility, whereas the release of niobium and selenium may be solubility–limited [15]. The minimum solubilities for these elements inside the copper canister in high alkaline pounding water is 2.7×10^{-3} mol/l for niobium and 2.0×10^{-7} mol/l for selenium. Iodine and selenium have not been expected to experience sorption, whereas cesium and niobium has been presumed to be somewhat retained by the buffer and backfill material (cesium and niobium lower limit K_d values 5.3 ml/g and 100 ml/g, respectively, for bentonite buffer) [15]. The elemental solubility and sorption is reflected in the hypothetical release rates of [135]Cs, [129]I, [94]Nb and [79]Se into the surface environment (soil rooting zone) in BSA modelling, where [129]I release was observed immediately after the final disposal and the rate increased with time [3]. [135]Cs, [94]Nb and [79]Se were expected to be released in the respective order one after the other beginning from 1500 years after the final disposal, and the release rate for all increased with time. Within these hypothetical scenarios for [135]Cs, [129]I, [94]Nb and [79]Se, the highest contribution to the radiation dose on the time scale used in the BSA calculations (0–10 000 years after the final disposal) was attributed to [129]I. Similarly, the impact of [135]Cs to radiation dose was systematically higher than the respective ones of [94]Nb and [79]Se. Table 1 combines the physical characteristics (half–life, decay mode and maximum energy), the BSA group and justification for BSA importance, as well as expected chemical forms of [135]Cs, [129]I, [93m,94]Nb and [79]Se in the repository conditions.

Table 1. *Elements investigated in this work and their significant radioisotopes in the final disposal of SNF. BSA importance and reasoning for the division as given in Posiva 2012 [15] is included in addition to formation mode, partition into disposal components (fuel, IRF, Zircaloy and other metallic components) and expected chemical forms in the repository conditions.*

Element (isotope) [17]	Half–life (a) [17]	Decay mode (maximum energy), decay product [17]	Formation mode	Expected chemical form in repository conditions [15]	Importance in BSA*[3]	Explanation for BSA importance [15]	Partition of mass (%) in final disposed components [15]
Cs (^{135}**Cs**)	2.3×10^6	100 % β⁻ (269 kev) ^{135}Ba	^{235}U fission (yield 6.5 %)	^{135}Cs⁺	High priority (I)	Long half-life, very high inventory in SNF	UO₂ matrix 95 % + IRF 5 %
I (^{129}**I**)	15.7×10^7	100 % β⁻ (154 kev) ^{129}Xe	^{235}U fission (yield 0.71 %)	^{129}I⁻	Top priority	Long half-life, no retention	UO₂ matrix 95 % + IRF 5 %
Nb (^{93m}**Nb**)	16	100 % IT ^{93}Nb	^{93}Nb activation, ^{235}U fission (yield 1.8×10^{-11} %), ^{93}Zr and ^{93}Mo decay	^{93m}Nb(OH)₅ or ^{93m}NbO₃⁻	High priority (I)	Short half-life, very high inventory; parent nuclide ^{93}Zr may act as a source →^{93m}Nb may become important if migration times are short	UO₂ matrix 0.1 % + Zircaloy cladding 94.9 % + other metallic parts 5 %
Nb (^{94}**Nb**)	2.03×10^4	100 % β⁻ (472 kev) ^{94}Mo	^{93}Nb activation, ^{235}U fission (yield 9.4×10^{-4} %)	^{94}Nb(OH)₅ or ^{94}NbO₃⁻	High priority (I)	Long half-life, high inventory	(see above)
Se (^{79}**Se**)	3.7×10^5	100 % β⁻ (151 kev) ^{79}Br	^{78}Se activation, ^{235}U fission (yield 0.044 %)	^{79}Se²⁻ (as H^{79}Se⁻)	High priority (II)	Long half-life, high inventory in SNF	UO₂ matrix 99.6 % + IRF 0.4 %

* Importance in BSA indicates the relevance of radionuclide according the possible dose it or its progeny nuclide causes to a man in different hypothetical radionuclide release scenarios. The division of high priority radionuclides into groups I–III is established based on their importance for SNF long–term safety and is used for sharing research resources for site investigations [3].

1.2 ENVIRONMENTAL CHEMISTRY OF CESIUM, IODINE, NIOBIUM AND SELENIUM

In this Chapter the basic principles of environmental chemistry and behaviour of cesium, iodine, niobium and selenium in soil–solution system is described and a survey into the characteristics of their speciation is given.

1.2.1 CESIUM

Cesium has only one stable isotope (^{133}Cs), but SNF contains three notable radioisotopes (^{134}Cs, ^{135}Cs, ^{137}Cs), from which the importance of relatively short–lived activation product ^{134}Cs ($t_{1/2}$ = 2.06 a) and fission product ^{137}Cs ($t_{1/2}$ = 30.1 a) is exceeded by the fission product ^{135}Cs ($t_{1/2}$ = 2.3×10^6 a) by its long half–life and high content in the SNF [3,17].

Cesium (Z = 55) is an alkali metal being the rarest among them. The electron configuration and electronegativity of cesium on Pauling's scale are [Xe]6s^1 and 0.79, respectively. Cesium ionizes eagerly to receive an octet configuration on its outermost electron shell upon giving up one electron. Thus, the only oxidation state of cesium is +I, at which it forms the hydrated Cs$^+$ cation. The speciation of cesium is independent of changes in solution pH or E$_h$ which makes Cs$^+$ cation a stable and sole form in the E$_h$–pH conditions relevant to soils and solutions [18].

The average concentration of cesium in Earth's crust and European soil is 3 − 4 mg/kg [19,20]. As a trace element cesium does not form discrete minerals by itself, but can replace potassium e.g. in silicate minerals such as amphiboles, feldspars and micas [21]. In Olkiluoto soil cesium is mainly bound to mineral lattices (average 870 ± standard deviation (STDEV) of 680 mg/kg) and in a lesser extent found as an exchangeable cation (2.2 ± 0.1 mg/kg) [22]. The concentration of cesium in natural waters is typically low, and the maximum concentration in Olkiluoto soil water is 3.4 × 10^{-9} M [22].

The solution chemistry of cesium is controlled by its typically low concentration and potentially high solubility. Due to this, cesium does not form precipitates or sparingly soluble compounds, and neither does it hydrolyse [23]. Complexation with the typical complexing agents (e.g. OH$^-$, F$^-$, Cl$^-$, NO$_3^-$, SO$_4^{2-}$, CO$_3^{2-}$) met in the hydrosphere does not occur [21,23]. Cesium is effectively sorbed and desorbed on colloids of mineral origin, such as clay minerals, but it does not form intrinsic colloids on its own [24-27].

The mobility of cesium in soil is expected to be rather low due to its efficient retention on soil mineral matter and especially on clay minerals and clay sized particles [28-30]. Retention on SOM (soil organic matter) is of lesser importance. Sorption processes of cesium are further discussed in Chapter 1.3.2.

1.2.2 IODINE

For iodine (Z = 53), the only stable isotope is [127]I, whilst the most important one in SNF is fission product [129]I ($t_{1/2}$ = 15.7 × 10^{6} a). In addition to human nuclear practises, this radionuclide is produced naturally in small quantities in the upper atmosphere through the activation of [128]Xe by cosmic ray interactions and spontaneous and thermal neutron fission of natural [235]U [31].

Iodine is an essential micronutrient for humans and animals and is needed in the proper functioning of thyroid gland and production of thyroid hormones [32]. It is a halogen with electron configuration of $[Kr]5s^24d^{10}5p^5$ and electronegativity of 2.66 on Pauling's scale. Iodine misses only one electron from its outmost electron shell to receive an octet configuration, and thus it readily forms a negative ion with the charge of −I (I^-, $[Kr]5s^24d^{10}5p^6$). However, iodine can also be present on other oxidation states including 0 (I_2), +I (HIO, $[Kr]5s^24d^{10}5p^4$) and +V (IO_3^-, $[Kr]5s^24d^{10}$).

Iodine forms a variety of compounds with diverse properties, making it a widespread element within the atmosphere, lithosphere and biosphere [33-35]. Its average content in topsoil (0−25 cm; excluding humus) of Europe is 3.94 mg/kg [20]. In soils iodine is highly associated with organic matter (OM) [36-38], as also in Olkiluoto, where the highest concentrations were determined for humus (average 15.5 ± 9.3 mg/kg) [39]. In Olkiluoto mineral soil, iodine concentration decreased with depth from 0.73 ± 0.65 mg/kg at 10−50 cm to < 0.21 ± 0.07 mg/kg at the depths below 200 cm, and averaged to a value of 0.46 ± 0.47 mg/kg [39]. Olkiluoto groundwater contains iodine in the range of 7.8 × 10^{-8} M − 1.5 × 10^{-6} M, the average value being 5.9 × 10^{-7} M [40]. Typically iodine forms readily soluble compounds, but as exceptions, the iodides of silver and mercury are sparingly soluble [18].

In soil−solution systems the speciation and behaviour of iodine is primarily governed by redox potential and microbial activity [33,35,36,41-43]. In general, iodate (IO_3^-) is considered as the dominant form in oxidising soil environments, and is displaced by iodide (I^-) in somewhat less oxidising conditions. However, iodide is expected to be the major species in most naturally encountered soil−solution systems due to its stability on a wide E_h−pH range (Figure 1) [44]. In addition to iodate and iodide, formation of molecular iodine (I_2) and different organo−iodine forms including volatile methyl iodine (CH_3I) has been observed [45,46].
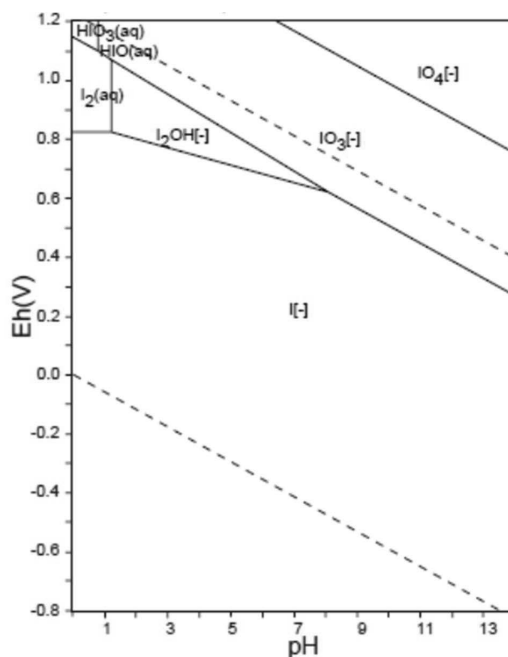
Figure 1. E_h–pH diagram of iodine [44]. The dashed lines present the stability limits of water (lower line: decomposition of water into hydrogen gas and upper limit: decomposition of water into oxygen gas).

The species transformations of iodate and iodide and iodination of organic matter are highly linked to the presence and action of soil microbes [36,42,43,47]. The formation of rather ubiquitous organo–iodine (OM−I) compounds in soils proceeds as monosubstitution of a proton in ortho- or para–position of an aromatic compound, preferably aromatic phenol, by reactive iodine (HIO or I_2) in enzymatically, peroxidase or metal oxide assisted iodination reaction leading to formation of a strong, covalent C−I bond [38,47-52]. The formation of OM−I compounds is favoured in low pH values also favouring the formation of I_2 in abiotic and biotic electron transfer reactions by quinolic moieties, free radicals and peroxidase enzymes [49,53-56]. The iodination of organic matter is limited by aromatic carbon content [47,57]. In the presence of sufficient amounts of aromatic carbon, OM−I compounds are formed irrespective of the initial chemical form of iodine (iodate or iodide) [42,47,48,58], whereas in environments where aromatic carbon supply is limited, iodate reduction into iodide has been obseved [47]. OM−I compounds can easily be decomposed in reducing soil conditions [43,52,59], but otherwise these compounds are presumed stable since the covalent C−I bond can only be broken to aliphatic chains by stronger nucleophiles (e.g. sulphide or thiosulphate) or iodine is replaced by stronger electrophiles (e.g. fluoride) [52].

Apart from the OM rich humus layer, the retention of iodine in soil is expected to be low and affected by factors such as solution composition and pH, soil mineralogy and content of weakly crystalline Al and Fe oxides [34,36-38,56,60]. Sorption processes of iodine are further discussed in Chapter 1.3.3.

1.2.3 NIOBIUM

Unlike other studied elements, niobium (Z = 41) has two important radioisotopes in SNF, namely ^{93m}Nb ($t_{1/2}$ = 16 a) and ^{94}Nb ($t_{1/2}$ = 2.03 × 10^4 a) [3]. Both are activation products formed by neutron irradiation from the only stable isotope of niobium, ^{93}Nb, by the reaction of ^{93}Nb(n,n) ^{93m}Nb and ^{93}Nb (n,γ) ^{94}Nb [61]. Stable ^{93}Nb is found as an impurity in structural components of nuclear reactor pressure vessel and small quantities of ^{93}Nb is added into Zircaloy alloy to improve its strength in high temperatures and to inhibit intercrystalline corrosion [61]. Even though ^{93m}Nb has relatively short half–life of 16 a, its importance arises from its continuous formation from its long–lived parent nuclides ^{93}Zr ($t_{1/2}$ = 1.53 × 10^6 a) and ^{93}Mo ($t_{1/2}$ = 4.0 × 10^3 a) [17].

Niobium is a transition metal belonging to 5th group in the periodic table of elements together with vanadium and tantalum. The electronegativity of niobium on Pauling's scale is 1.60, and its electron configuration is [Kr]4d^{4}5s^1. Niobium has four oxidation states, namely +II ([Kr]4d^3), +III ([Kr]4d^2), +IV ([Kr]4d^1) and +V ([Kr]), of which the most stable is +V (NbO_3^- or $Nb(OH)_5$) [62]. Niobium is typically encountered at this oxidation state in soils and solutions [61,63].

Niobium is a lithophilic element and is found with an average content of 11.5 mg/kg in the upper continental crust [64]. In Europe, the average niobium content in topsoil is 9.7 mg/kg, whilst the range encountered in Finland is 4.9 – 9.7 mg/kg [20]. Pyroxenes, amphiboles, micas, ilmenite and magnetite contain niobium at trace levels [65], whereas columbite (($Fe,Mn)Nb_2O_6$) and edgarite ($FeNb_2S_6$) metal ores can contain up to 53 % of niobium [65-67]. The chemical form of niobium in minerals is proposed to be niobite (Nb_2O_6) or niobate (Nb_2O_5) based complex oxides [61].

Oxidation state +V for niobium is relatively stable at redox conditions differing from reducing to oxidative [61,63]. Niobium readily forms complex ions in solutions due to its high charge. In acidic solutions niobium exists as niobyl oxocation (NbO_3^+), whereas from slightly acidic to neutral solutions neutral species ($HNbO_3$ or $Nb(OH)_5$) are formed. Anionic forms start to dominate niobium speciation at pH values higher than approximately of 6.5 (Figure 2). In solutions, only a small fraction of niobium is expected to occur as solute as the majority is retained by colloids generated from iron hydroxide, organic matter or clay minerals [68-70]. Niobium also has a high tendency to form sparingly soluble compounds with alkali earth and other metal cations, examples being $Ca(NbO_3)_2$ and $Fe(NbO_3)_2$; be complexed with fluoride, citrate and oxalate ions; and be retained very efficiently on soil mineral matter and

OM [61,69-74]. These factors would indicate niobium being relatively immobile in soils. Sorption processes of niobium are further discussed in Chapter 1.3.3.
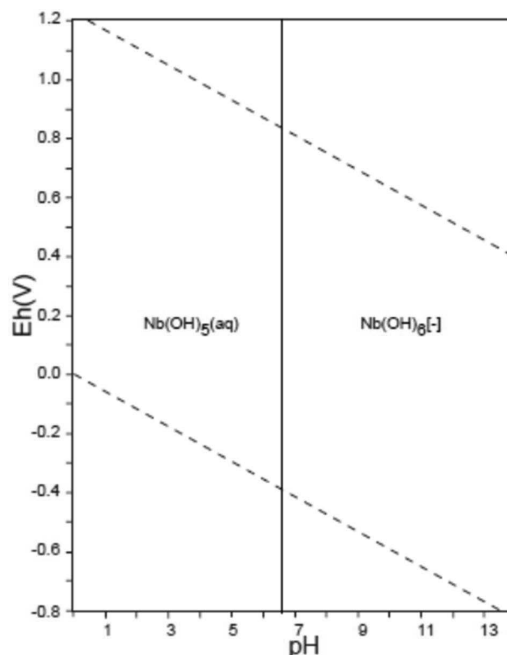

Figure 2. E_h–pH diagram of niobium [44]. The dashed line presents the stability limits of water (lower line: decomposition of water into hydrogen gas and upper limit: decomposition of water into oxygen gas).

1.2.4   SELENIUM

Selenium (Z = 34) has five stable isotopes ([74]Se abundancy 0.89 %; [76]Se 9.37 %; [77]Se 7.63 %; [78]Se 23.77 %; [80]Se 49.61%), and very long–lived radioisotope [82]Se ($t_{1/2}$ = 1.08 × 10^{20} a, abundancy 8.73 %) which is practically considered as stable. In the biosphere safey assessment of SNF, the most important isotope of selenium is [79]Se ($t_{1/2}$ = 3.7 × 10^5 a). Even though small quantities of [79]Se is formed in the fission of [235]U (yield 0.044 %), the main route to its formation is neutron irradiation induced activation of stable [78]Se by the reaction [78]Se (n,γ)[79]Se in nuclear fuel and reactor construction materials.

Selenium is a non–metal with electron configuration of $[Ar]3d^{10}4s^24p^4$ and electronegativity of 2.55 on Pauling's scale. It belongs to the 16th group of elements together with oxygen, sulphur and tellurium, and its chemistry bears considerable resemblance to that of sulphur. Selenium can be present on multiple different oxidation states the most common ones being –II (H_2Se, $[Ar]3d^{10}4s^24p^6$), 0 (Se), +IV (SeO_3^{2-}, $[Ar]3d^{10}4s^2$) and +VI (SeO_4^{2-}, $[Ar]3d^{10}$).

Selenium is an essential trace nutrient to man and needed with respect to its e.g. antioxidative nature, necessity in the proper functioning of the immune system and in reducing the risk of cardiovascular diseases and cancer [75]. Selenium dietary intake is directly affected by soil selenium status and is characterized by a narrow range between deficient and toxicant dose [76]. The average topsoil selenium content is estimated to be 0.33 mg/kg on a world-wide basis [77], whereas the typical range is 0.01 – 2 mg/kg even though concentrations as high as of 1250 mg/kg can be met in seleniferous soils [78]. Soil and groundwater contamination with stable selenium is produced in multiple human activities such as coal and fossil fuel combustion, mining, refining of crude oil and agricultural irrigation of selenium rich soils [76].

Young, relatively unweathered, naturally acidic and Al and Fe oxide rich Finnish soils have naturally low content of plant available selenium [79,80]. In Olkiluoto soil, selenium is mainly found in exchangeable fraction (average 34.5 ± 18.1 mg/kg) and as bound to Fe and Mn oxides (average 18.4 ± 11.3 mg/kg) [22]. Selenium content in Olkiluoto humus (average 33.5 ± 29.8 mg/kg) is approximately 2.4–fold compared with mineral soil (average 13.7 ± 13.1 mg/kg), where the concentration remains approximately the same (13.7 ± 13.1 mg/kg) irrespective of soil depth [22]. The concentration of selenium in Olkiluoto soil solution is very low at $<6.3 \times 10^{-8}$ M [40].

Selenium is a chalcophilic element and easily replaces sulphur in sulphide minerals, such as pyrite (FeS_2), chalcopyrite ($CuFeS_2$), pyrrhotite ($Fe_{1-x}S$) and sphalerite (($Zn,Fe)S$) [20]. Other less common selenium minerals are known, these including crookesite (($Cu,Tl,Ag)_2Se$), berzelianite (Cu_2Se) and tiemannite ($HgSe$).

Selenium species transformations in soils and sediments are often slow reactions mediated by soil microbes or abiotic electron transfers. In well-oxidised environments, the most frequently encountered inorganic Se species is selenate (SeO_4^{2-}) and selenite (SeO_3^{2-}) in somewhat less oxidizing conditions (Figure 3). In reducing soil conditions elemental selenium is formed, whereas selenides (H_2Se or insoluble metal selenides) are produced only in highly reducing environments [81]. Oxidation of the reduced selenium forms (elemental selenium and selenides) are often slow due to their low solubility and low redox potentials of formation [82,83]. The oxidation reactions give a mixture of selenite and selenate in varying proportions depending on the prevailing soil redox potential and pH [84], whereas the reduction of selenate into selenite and to more reduced forms proceeds straightforward and can be finished within days depending on soil reduction status [83-86].

Soil microbes have established to have an important role in selenium biogeochemistry, speciation and distribution in soils [87]. The capability of soil microbes to reduce selenium by using it as terminal electron acceptor in their energy production is more common than the ability to oxidise. Reducers are, for instance, *Wolinella succinogenes* [88], *Pseudomonas stutzeri* [89] and *Shewanella putrefaciens* [90], whereas *Thiobacillus* and *Leptothrix* are examples of selenium oxidisers [91]. In addition to microbial reduction and

oxidation of selenium [82,88-91], species transformations can proceed through an abiotic route. Reduction–oxidation reactions take place as homogenous aqueous phase reactions or as heterogeneous surface reactions in the presence of Fe(II) on clay surfaces, Fe(II,III) –bearing minerals, pyrite or chalcopyrite, all leading to formation of Se(0) and/or Fe(II)selenides [92-96]. However, the abiotic oxidation/reduction reactions are of less importance compared with the biotic route [82], which also yields organo–selenium (OM–Se) compounds through microbial assimilation of selenium into SOM [81]. In this process selenate and selenite are reduced to selenide and incorporated into organic molecules forming groups of seleno-amino acids (e.g. selenocysteine and selenomethionine), methyl selenides (e.g. $(CH_3)_2Se$) and methyl selenones (e.g. $(CH_3)_2SeO_2$) [81].
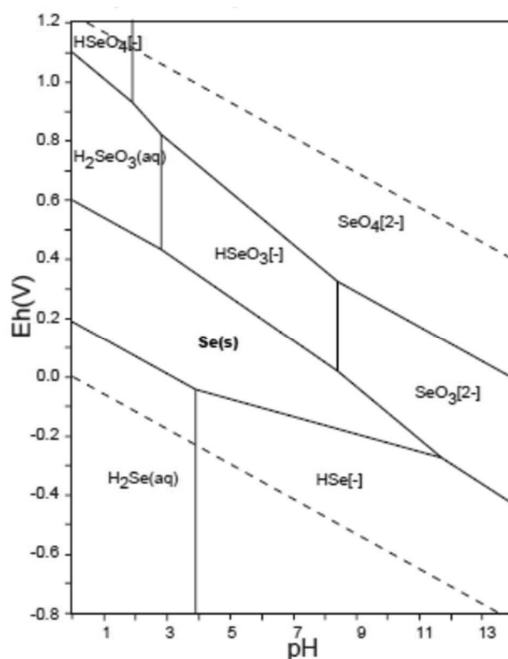
Figure 3. Eh–pH diagram of selenium [44]. The dashed line presents the stability limits of water (lower line: decomposition of water into hydrogen gas and upper limit: decomposition of water into oxygen gas).

Of the various chemical forms of selenium, the oxyanions selenate and selenite are considered to be the most mobile ones and biogeochemically significant. Both species are retained in OM rich soil layers, whereas in mineral soil selenite is held in a more stronger fashion than selenate [97,98] [99,100]. Other factors affecting the behaviour of selenium in soils include solution composition and pH, soil mineralogy and content of weakly crystalline Al and

Fe oxides [80,98-102]. Sorption processes of selenium are further discussed in Chapter 1.3.3.

1.3 SORPTION PROCESSES

In soils, cationic and anionic moieties are retained by functional groups present in OM and mineral surfaces. Sorption reactions are typically dependent on the characteristics and composition of the retaining phase (e.g. concentration, type and distribution of sorption sites), solutes (e.g. oxidation state, chemical form) and soil solution (e.g. pH and ionic strength). Two sorption mechanisms has been identified: outer sphere complexation (ion exchange) and inner sphere complexation. Of these two, outer sphere complexation is always non–specific and similarly charged ions present in the solution compete for the same sites. Inner sphere complexation is limited to a certain groups of substances fulfilling the terms for specific sorption provided by the sorbent phase.

1.3.1 SORPTION CHARACTERISTICS OF SOIL ORGANIC MATTER AND SOIL INORGANIC COMPONENTS

Organic matter

Humus, or soil organic matter (SOM), consists of two groups of compounds, namely nonhumic and humic substances. As a separating factor between the groups, nonhumic substances have chemically identifiable structure and they can be recognised belonging to a certain biochemical class. For humic substances, the identification of functional groups is achievable, whereas the same does not apply for their structure. Examples of nonhumic substances are simple carbohydrates and polysaccharides, amino sugars and amino acids, peptides and phospholidips [21,103]. Humic substances are generally considered being extremely complex in their structure, heterogenous and relatively resistant to microbial breakdown. These substances can be divided into three groups based on their solubilities in acidic and alkaline solutions: fulvic acids are soluble in both solutions, humic acids only in alkaline solutions and humins are insoluble in both.

Typically SOM holds a considerable fraction of soil cation exchange capacity (CEC). This is because SOM has a broad spectrum of neutral, acidic and basic functional groups participating in the retention reactions of elements [21,103]. The vast majority of the SOM functional groups contain oxygen and are neutral (not ionizing but possibly polar) or acidic (negative charge development through deprotonation, Figure 4) in their character [21]. Examples of neutral groups are, for instance, carbonyl groups, aliphatic–OH groups, aliphatic and aromatic ether; whereas carboxyl groups, enol groups and

phenolic–OH groups present the acidic ones [21]. Basic (positive charge development through protonation, Figure 4) groups typically contain nitrogen, and examples include amine, amide and imide groups and aromatic ring nitrogen, e.g. pyridine [21].

SOM functional groups are able to attract cations or anions from the solution upon charge formation. In acidic functional groups, e.g. in –COOH, this is achieved by dissociating a proton to receive negative charge (e.g. –COO$^-$). The proton dissociation of the functional groups, and thus also their ability to attract cations from the solution, increases with pH; at pH < pK$_a$ the fraction of protonated groups exceeds the fraction of dissociated ones, at pH = pK$_a$ the concentrations are equal, and at pH > pK$_a$ the dissociated forms overcome the protonated ones. The acidic functional groups of SOM are weak acids having their pK$_a$ values in the range of 0–14 [21]. For example, the pK$_a$ of carboxyl group is approximately 3, indicating it to be in its dissociated form (–COO$^-$) basically on the whole environmentally significant pH range, whereas the respective for phenolic–OH is about 9, causing it to be in neutral form throughout the environmental pH range [103]. Also, the protonation of basic SOM functional groups shows dependence on their pK$_b$ (range 0–14) values, and the protonation degree increases with decreasing pH. Thus, the electrostatic attraction between positively charged functional groups and negatively charged ions from the solution is higher in the acidic pH range than in the alkaline one, whereas the opposite is true for cations. The retention of anions and cations by SOM takes place through unspecific outer sphere complexation excluding H$^+$ ions, which are specifically retained [21]. The affinity of outer sphere complexed ions on SOM functional groups increases with increasing charge/radius ratio (i.e. increase in ion charge density).

Acidic functional groups of SOM
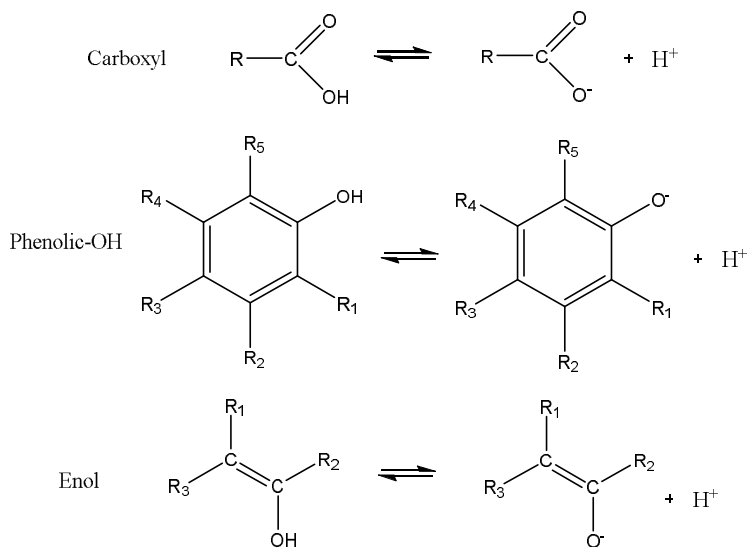
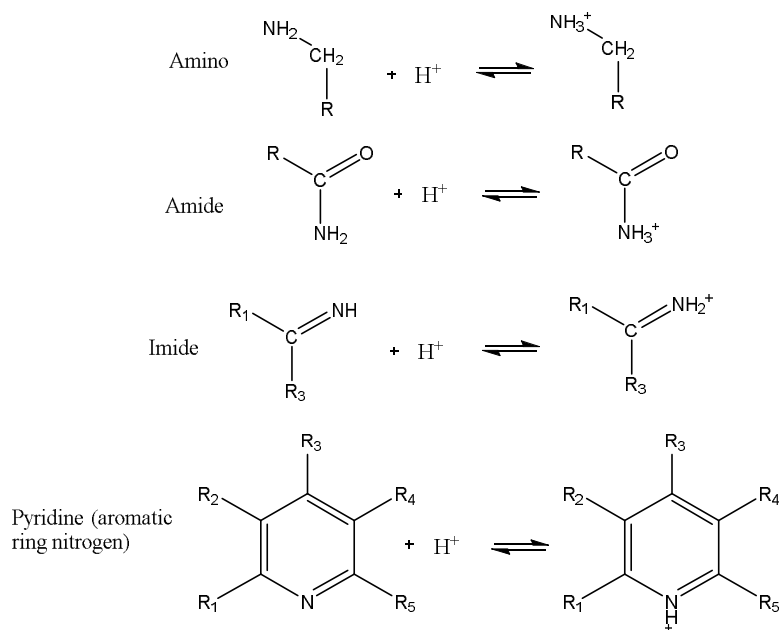**Basic functional groups of SOM**

Figure 4. Acid dissociation reactions of acidic (carboxyl, phenolic–OH and enol) functional groups and protonation reactions of basic (amino, amide, imide and aromatic ring nitrogen) functional groups present in SOM (adapted from [21]).

Minerals

Minerals are soil inorganic components that can either be crystalline and have a continuous and ordered three dimensional crystal structure or amorphous, when the ordered arrangement of atoms is missing [21]. Mineral surfaces can exhibit retention of ions from soil solution depending on mineral surface properties, i.e. the type and concentration of functional groups, in addition to the characteristics of the solutes themselves. As depicted in Figure 5, mineral surface generally attracts negatively charged anions in solutions with pH lower than the pH_{pzc} (pH point of zero charge) of the mineral [21]. In these circumstances the surface has higher concentration of protonated (e.g. $M-OH_2^+$, where M= central metal cation such as Al, Fe, Mn, Mg or Si) surface functional groups than deprotonated ($M-O^-$) ones, thus exhibiting positive charge. When solution pH rises, the faction of protonated groups declines (and the fraction of deprotonated groups can increase) to the point where the concentration of the oppositely charged groups are equal. This pH, where the mineral surface has neutral charge, is termed as pH_{pzc} of the mineral. With solution pH further rising, the fraction of deprotonated surface functional groups increases leading to an increase in negative surface charge and enhanced attraction of cations from the solution.

$$pH<pH_{pzc} \qquad\qquad pH=pH_{pzc} \qquad\qquad pH>pH_{pzc}$$

$$M\text{-}OH_2^+ \quad \underset{+\,H^+}{\overset{-\,H^+}{\rightleftharpoons}} \quad M\text{-}OH \quad \underset{+\,H^+}{\overset{-\,H^+}{\rightleftharpoons}} \quad M\text{-}O^-$$

anion retention   cation retention
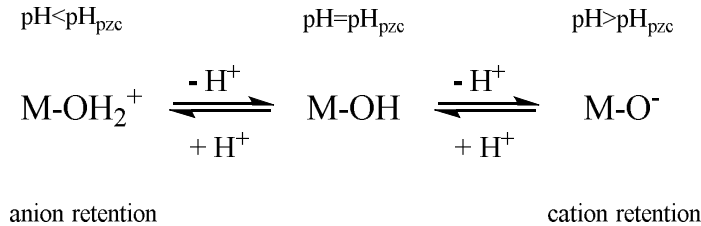
Figure 5. The effect of solution pH on the deprotonation and protonation of surface hydroxyl groups (M=central metal cation to which −OH group is attached to) (adapted from [21]).

Retention mechanisms of ions include ion exchange (outer sphere complexation) when the interaction is based on the electrostatic attractions (dipole–dipole, ion–dipole, van der Waals forces) between oppositely charged solutes and mineral surface functional groups. The solutes have a certain number of water molecules surrounding them in the primary hydration water shell in a manner that the dipole of the water molecules oriented towards the solute is opposite to the solute's own charge. This leads to a minimum thickness of one water molecule (0.3 nm) separating the solute and the mineral surface. In inner sphere complexation, there is no water molecules between the participants as part of the hydration water shell of the ion is lost when a direct chemical bond is formed [21,104]. For anions of weak acids, a chemical bond is formed between oxyanion's oxygen atom and surface metal cation, whereas for solute cations, the situation is opposite as the bond

formation involves surface oxygen atom and the solute metal cation. Oxyanions retained by inner sphere complexation include e.g. arsenate, borate, carbonate, chromate, molybdate, phosphate, silicate, selenite and selenate [21]. Inner sphere complexation is typically considered as a stronger retention mechanism of anions than outer sphere complexation, since the retained species are replaced only with oxyanions of a higher pK$_a$ value (i.e. weaker acid). For outer sphere complexation, changes in soil solution composition and pH can lead to desorption reactions. In addition to mineral surfaces, retention processes can occur in interlayer spaces of certain clay and mica minerals. Figure 6 gives an illustration of cesium retention on muscovite surface through outer sphere complexation and in the interlayer space by inner sphere complexation. The outer and inner sphere complexation of anions are illustrated in Figure 7.

In addition to pH–dependent charge (Figure 5), clay (and mica) minerals carry also permanent negative charge resulting from isomorphic substitutions in the mineral lattice, when cations (e.g. Si^{4+}) are typically replaced with cations of a lower positive charge (e.g. Al^{3+}). The permanent negative structural charge is mainly balanced by exchangeable cations in the interlayer spaces of clay minerals. Depending on the location and extent of the charge deficiency, the interlayer expandability and characteristics of interlayer cations varies [21]. If the isomorphic substitution is in Si–tetrahedron relatively close to the interlayer, interlayer surface siloxane groups will develop high negative charge density leading to formation of strong surface complexes with cations (inner sphere complexes). If the origin of the permanent negative charge lies in the Al–octahedron, the siloxane groups will have lower charge density and weaker interaction strength (outer surface complexes) with hydrated interlayer cations [21].

The acidity of surface hydroxyl groups differs depending on the number of structural metal (M) atoms which it is bound to, the M–OH bond strength and the electronegativity of the central metal cation [21]. With these variables decreasing in their value, the acidity of the M–OH group decreases, i.e. the ability of the functional group to remain protonated at higher pH values increases. As the functional groups remain protonated at elevated pH values, their tendency to retain anions is higher than the respective of ones having lower pK$_a$ values. As an example, Si–OH, a typical hydroxyl group met on soil minerals, has pK$_a$ value of approximately 3 and remains in its deprotonated form (Si–O⁻) on the environmentally relevant pH scale exhibiting only cation retention. Al–OH and Fe–OH groups, on the other hand, have pK$_a$ values of approximately 8–9 and play an important role both in anion inner and outer sphere complexation on a wide pH range in soils [21].

In addition to soil minerals, weakly crystalline aluminium and iron oxides bear a significant proportion of reactive Al–OH and Fe–OH groups on their surfaces. These substances are highly important for soil sorption of oxyanions [37,38,105,106]. However, if soil redox potential is low enough (from +80 mV to +110 mV), Fe(III) can be reduced to Fe(II) leading to sequential dissolution of the

iron oxide and liberation of the retained oxyanions (e.g. selenite) into the solution [107]. These liberated oxyanions can be re–sorbed on weakly crystalline Al oxide, since this element is not redox sensitive and thus fluctuation in soil redox potential does not affect the retentive properties of Al [21,107,108].

An indication of mineral surface reactivity towards oxyanions is possibly achievable from the knowledge of mineral atomic structure, when the mineral (Al+Fe):Si ratio is determined. Layer silicate minerals with 2:1 (Si–tetrahedral:Al–octahedral:Si–tetrahedral layer) structure have lower (Al+Fe):Si surface ratios than 1:1 (Si–tetrahedral:Al–octahedral layer) layer silicate minerals, and also have shown poorer retention of humic acids [109]. Since the retention of humic acids on mineral surface Al–OH and Fe–OH groups proceeds by inner sphere complexation, (Al+Fe):Si surface ratio can presumed to give a hint of oxyanion sorption tendency also for other minerals than 1:1 and 2:1 layer silicates. Minerals consisting mainly of SiO_2 (quartz, potassium feldspar and plagioclase), have surface (Al+Fe):Si ratios close to unity indicating possible low retention by inner sphere complexation. However, minerals possessing more structural Al+Fe (e.g. hornblende, hematite, chlorite), have higher (Al+Fe):Si surface ratio and thus offer more Al–OH and Fe–OH functional groups participating in the inner sphere complexation reactions.

1.3.2 CESIUM

Cesium is present in soils and solutions as a hydrated Cs^+ cation with a low charge and large size. Partly due to this, the main retention mechanism on mineral surfaces and SOM is outer sphere complexation. The efficiency of the retention depends on the characteristics of the sorbent (e.g. OM content, mineralogy, particle size) and solution (e.g. pH, Cs^+ and other cation concentration, ionic strength) [110-112].

Even though cesium is retained rather poorly on the majority of mineral surface sorption sites, e.g. Si–OH, Al–OH and Fe–OH groups situating on the outer surfaces and broken edges of mineral particles, specific retention of cesium takes place in the interlayer spaces of certain clay and mica minerals exhibiting high layer charge (e.g. illite, muscovite and biotite) [113]. These minerals can release their interlayer cations (K^+) into soil solution from the edges inwards as affected by mineral weathering or a decrease in soil solution K^+ concentration [113]. A wedge shaped area called FES (frayed edge site) is formed between the collapsed central core (containing interlayer K^+) with a thickness of 1.0 nm and an expanded layer part (interlayer K^+ lost) of 1.4 nm wide [113,114]. Cesium is preferred on these sites since it has such a low hydration energy (-264 kJ/mol for gaseous Cs^+), that the oxygen atoms of siloxane groups present in the interlayer surfaces and acting as hard Lewis bases, can displace the entire hydration water shell of Cs^+. As a result, Cs^+ forms a covalent bond with six oxygen atoms of siloxane ditrigonal cavity. When the FES site is occupied and the interlayer space from that place is collapsed, a

new FES site will be formed beside the old one. However, if the interlayer collapse is not induced, e.g. due to low Cs^+ concentration or presence of hydrated interlayer cations, Cs^+ cations remain as reversibly bound [115]. Even though cesium is specifically retained on the FES sites, K^+ and NH_4^+ have similar chemical properties and ion size as Cs^+, and are capable of competing for the FES sites [23,110,113]. However, the formation of NH_4^+ in soils requires NO_3^- reduction in decreased soil redox potentials (E_h < +300 mV), whereas soil solution K^+ concentration varies e.g. due to plant uptake, being still several orders of magnitudes higher than the respective of cesium (e.g. average K^+ concentration in Olkiluoto soil solution 1.5×10^{-4} M versus the maximum of 3.4×10^{-9} M for Cs^+) [19,22,116,117]. Strongly hydrated cations such as Na^+ and Ca^{2+} show no competition on the FES sites, and are exchanged from the sites by low hydration energy cations (e.g. Cs^+, Rb^+, K^+, NH_4^+) [110,113,118]. In soils, the concentration of the FES sites shows variation depending on factors such as soil formation processes, which affects the amount of micaceous minerals, their structural type and also their weathering degree [114]. The retention of cesium by outer and inner sphere complexation on muscovite is illustrated in Figure 6.

Because of the low retention of cesium on SOM by an outer sphere complexation reaction susceptible to competition of other soil solution cations (e.g. H^+, K^+, Na^+, Ca^{2+}, Mg^{2+}, Al^{3+}), it has been proposed that even small amounts of clay and mica minerals possessing cesium selective FES sites are behind the sorption of cesium in OM rich soil layers [10,119-122]. However, cesium retention on the FES sites can be hindered when clay and mica mineral interlayer spaces are occupied by fulvic acids or they are sterically blocked by organic macromolecules retained on the reactive anion exchange sites (mainly Al–OH) situating in the vicinity of the FES sites [21,30,123,124]. In addition to reactive –OH groups, OM compounds are also retained by siloxane surfaces of clay minerals, even though the interaction is of weaker strength than with –OH groups [124].
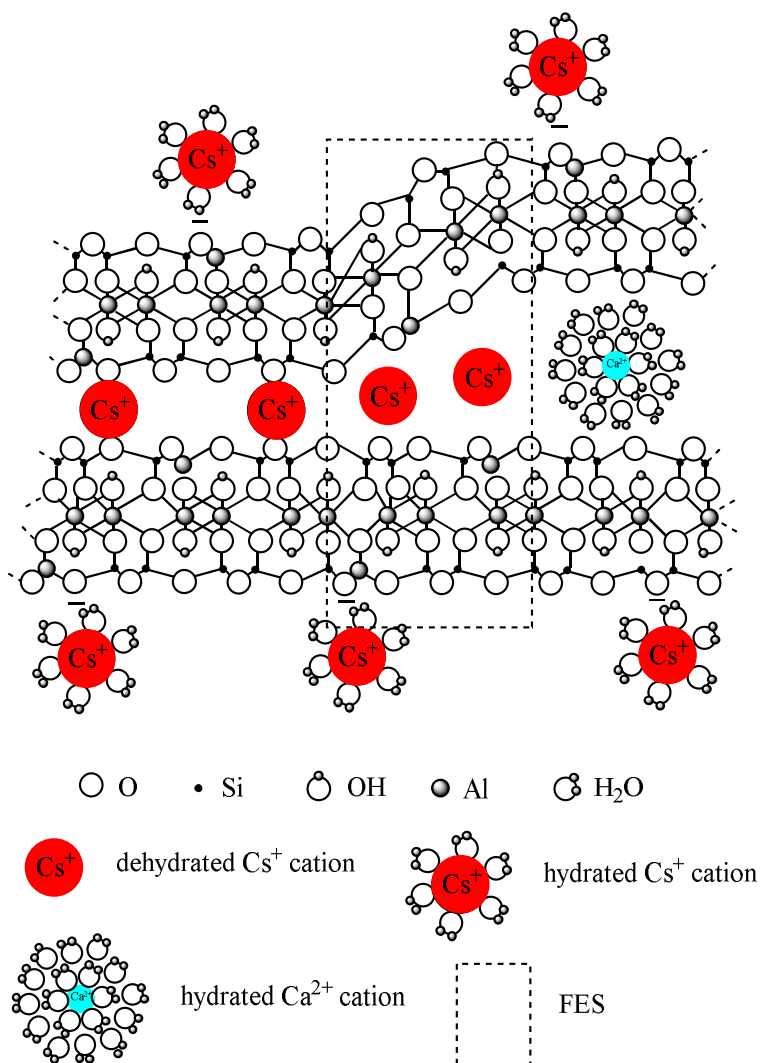
Figure 6. An illustration of the retention of hydrated Cs+ cation through electrostatic attraction with the negatively charged functional groups on the outer surface of muscovite (i.e. outer sphere complexation) and the specific retention of dehydrated Cs+ cations on the FES site in the muscovite interlayer space (highlighted by dashed line) (adapted from [21,114]). On the left side of FES, the retention of Cs+ cations has caused interlayer dehydration and collapse, whereas on the right side of FES strongly hydrated Ca2+ cation(s) keeps the interlayer in the expanded state.

1.3.3 IODINE, NIOBIUM AND SELENIUM

Variation in factors such as OM content, mineralogy and soil texture, time, microbiological activity, E_h–pH conditions and soil solution composition generate sorption decreasing or increasing effect for anions in soils [56,59,83,98,100,125-133]. Generally, SOM is known to be an important sink for anionic moieties of iodine and selenium due to the multiplicity of functional groups present, their relatively high concentration and ability to remain protonated on a wide pH scale [21,36-38,56,99,103,130,134,135]. The importance of SOM as a retentive medium is higher for iodine than for selenium, as Al and Fe bearing mineral phases mingled within the OM matrix may account for selenium sorption even in OM rich layers [36,38,100]. It has also been suggested that OM rich soil layers are important for the retention of niobium in soils [73].

The sorption of anions on the protonated functional groups of SOM is by outer sphere complexation and is affected by pH and concentration of other anions (e.g. PO_4^{3-}, CO_3^{2-}, SO_4^{2-}) in the solution [37,38,98,136]. Solution pH affects directly the protonation degree of SOM functional groups and possibly also the speciation of elements of interest [21,44,103].

Association of iodine and selenium on OM may also be caused by other means than outer sphere complexation. Soil microbes have been found to induce speciation changes of iodine and selenium and their subsequent incorporation into OM [36,42,43,47,48,58,81,82,89-91,129,130], discussed in more detail in Chapter 1.2.2 for iodine and 1.2.4 for selenium. In fact, the tendency of OM to serve as a sink for iodine is preferably caused by the formation of OM–I compounds than sorption [35,48,137].

Soil minerals exhibit only very small anion exchange capacity being at its largest at the very acidic range of environmentally encountered pH values. As the pH increases and the proportion of protonated surface functional groups ($M–OH_2^+$) decreases (Figure 5), the fraction of anions retained by outer sphere complexation diminishes. Since outer sphere complexation is the main retention mechanism for iodide and selenate, their retention in soil typical pH values (neutral to slightly alkaline) is considered to be low [34,60,106,138-140]. Selenate has also been observed to form inner sphere complexes with hydrous ferric oxide, goethite, hematite and corundum [105,106]. The retention of iodate, selenite and also possibly of niobate, proceeds as a mixture of outer and inner sphere complexation [21,102,105,128,139,141]. In soil–soil solution systems anions retained by outer and inner sphere complexation are competing for the same retention sites (Al–OH and Fe–OH), and typically the formation of inner sphere complexes is favoured [21]. Furthermore, inner sphere complexation can take place on surfaces having positive, neutral or negative surface charge, whilst positive surface charge is favoured as H_2O makes an excellent leaving group. Figure 7 illustrates the retention of anions by outer (I^-, SeO_4^{2-}) and inner ($HSeO_3^-$) sphere complexation on muscovite surface.
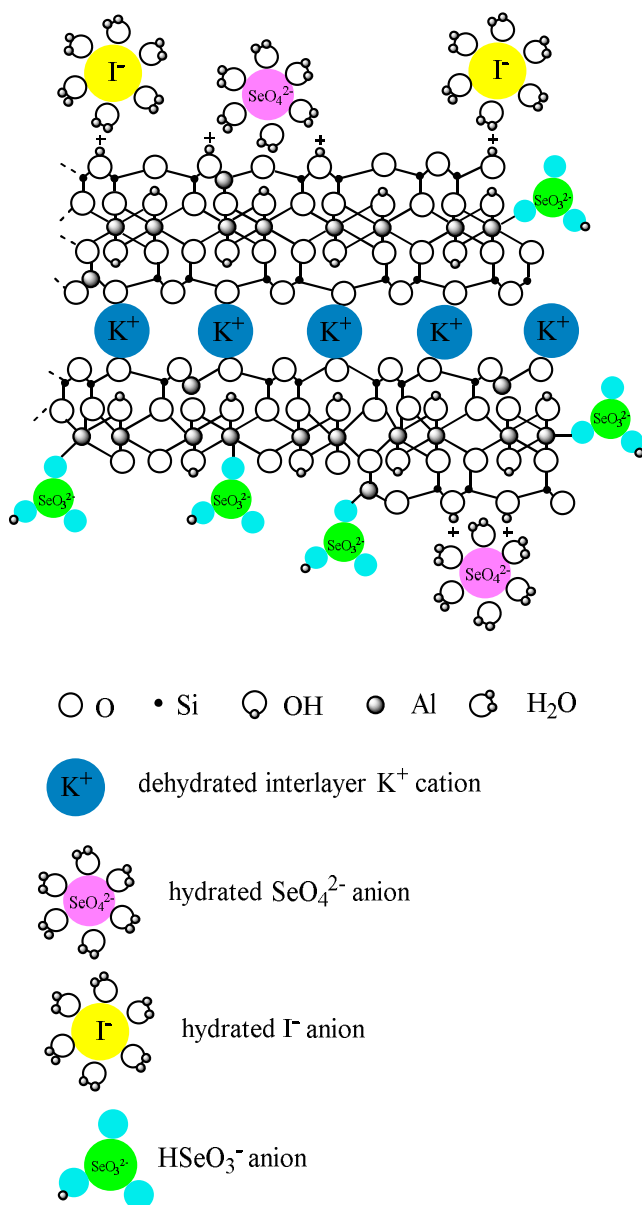
Figure 7. An illustration of the retention of hydrated I^- and SeO_4^{2-} anions through electrostatic interaction with the positively charged functional groups on the outer surface of muscovite (i.e. ion exchange, outer sphere complexation) and the specific sorption of $HSeO_3^-$ anions by the formation of a chemical bond between selenite's oxygen atom and surface Al atom through a ligand exchange mechanism (inner sphere complexation) (adapted from [21,142]).

In inner sphere complexation a direct chemical bond is formed between oxygen atom from oxyanion and structural surface metal atom. The reaction is proposed to proceed as a nucleophilic S_N2-i-substitution (Figure 8) [142], in which a hydrogen bond is formed between surface –OH group and hydrogen of the oxyanion, e.g. $HSeO_3^-$. In the mechanism, free electron pair on oxyanion's oxygen is attracted towards surface metal cation and –OH (or H_2O) ligand is cleaved from the surface metal. A new chemical bond with covalent nature is formed between surface metal and oxyanion's oxygen atom [21,142]. Inner sphere complexes are stable and relatively difficult to break. In theory, oxyanion retained by inner sphere complexation can be replaced by one with a higher pK_a value (i.e. weaker acid) [21]. For specifically retained species studied in this work, bonding strength would theoretically increase in the order of $HSeO_4^-$ (pK_{a1} -3) > IO_3^- (pK_a 0.80) > SeO_4^{2-} (pK_{a2} 1.7) > $HSeO_3^-$ (pK_{a1} 2.6) > $Nb(OH)_6^-$ (pK_{a1} 7.3) > SeO_3^{2-} (pK_{a2} 8.4) > $Nb(OH)_7^{2-}$ (pK_{a2} 8.8) [105,106,143,144].

Inner sphere complexation can be monodentate or bidentate in mononuclear or binuclear fashion. In monodentate retention one place of the coordination sphere of the oxyanion is occupied by surface metal atom, whereas in bidentate the number is two. In mononuclear retention oxyanion is bonded to one surface metal atom, and respectively in binuclear fashion bonding takes place with two separate surface metal atoms. For example, selenite is known to form mononuclear–monodentate inner sphere complexes on hematite and magnetite surfaces [96,140], either mononuclear–monodentate or binuclear–bidentate with goethite [96,97,139] and binuclear–bidentate on hydrous aluminium oxide [105].
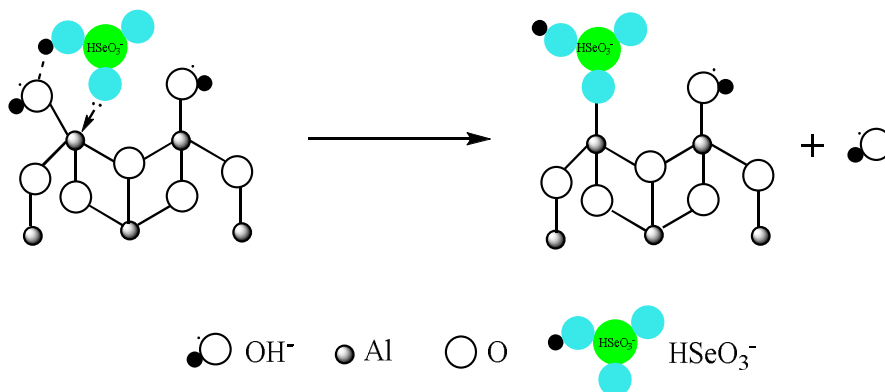
Figure 8. Nucleophilic S_N2-i-substitution of surface –OH group by $HSeO_3^-$ ion and formation of mononuclear monodentate $HSeO_3^{2-}$ inner sphere complex with surface Al atom (adapted from [142]). Dashed line (---) represents hydrogen bond and arrow (⟶) the ions between which the new bond is formed.

In addition to aluminium and iron, the presence of certain elements in the mineral structure of the sorbing material has been noticed to affect the retention of iodine and selenium. For example, iron(II) bearing minerals, such

as pyrite and biotite, are expected to exhibit increased retention of iodine and selenium by means of reduction reactions, such as $IO_3^- \rightarrow I_2$ or I^- and $SeO_3^{2-} \rightarrow$ Se(0), Se^{-2} [33,92-94,96,145]. Furthermore, the formation of insoluble iodides with structural metal cations such as Hg^{2+} found in cinnabar (HgS) [146], can increase the retention of iodine on the solid phase. However, the occurrence of cinnabar is linked to mercury deposits and as such has no meaning for Olkiluoto soils [77].

1.4 HPLC–ICP-MS AS A SPECIATION ANALYSIS TECHNIQUE

HPLC (high–performance liquid chromatography) is a widely used method for the separation, identification and quantification of analytes from solutions [147-149]. In HPLC, the 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 column and conditions. The basic principle is the use of pumps to pass pressurised eluent (mobile phase; 50–350 bar) containing the analytes of the sample through a separation column (stationary phase) and further transportation to detector, where the individual analytes are identified and quantified according their retention time and concentration against known standards. The separation modes include, for example, reversed–phase chromatography (RP; separation achieved through partition of the analytes between non–polar stationary phase and polar moving phase), size exclusion chromatography (SEC; analytes are separated according their size in porous stationary phase), and ion–exchange chromatography (IEC; separation by different interaction strength of charged analytes with the charged stationary phase). IEC is further divided into cation–exchange and anion–exchange chromatography depending on the charge of the separated analytes. Stationary phase is typically crosslinked styrene or latex and functional groups used in anion separations are positively charged primary or quaternary amines, whereas carboxylic and sulfonic acid groups are applied as weak and strong cation–exchange groups, respectively. Analyte retention is based on the affinity of different ions for the functional groups and on eluent parameters such as pH, counterion type and ionic strength [150]. The used eluents can be acidic or alkaline depending on the specifications of the column material and functional groups, and contain organic solvents to improve the separation efficiency [147].

In ICP-MS (inductively coupled plasma mass spectrometry), liquid sample is transformed into fine aerosols, ionised in plasma and separated in mass analyser according ion's mass to charge ratio [150]. Ions having the selected m/Z ratio are directed to detector, where ions are converted to electronical signal that the data-handling program can transform into concentration. ICP-MS can be used in the measurement of multiple different elements. However, certain disadvantages occur as for selenium the measurement of its most abundant

isotope (^{80}Se; 49.61 %) is useless due to formation of matrix interference $^{40}Ar_2^+$ dimer [151]. When reaction/collision cell is applied in the measurement, the formation of polyatomic spectral interferences generated from plasma gas, solvent, and matrix-derived ions can be reduced [150]. In these specifically designed cells the interference ions are collided with reaction gas (e.g. O_2, He, H_2) molecules leading to formation of noninterfering species. Another way is to collide analytes with reaction gas and have analyte molecules at a mass number with no major interferences.

When HPLC and ICP-MS are combined, HPLC offers efficient separation of different species and ICP-MS multielement measurements with fast analysis, low detection limits (even ng/l scale) and differentiation between isotopes [147-150]. As such, HPLC–ICP-MS has a wide range of applications in speciation analysis e.g. of iodide, arsenic and selenium from soil extracts and numerous type of water samples (e.g. rain, seawater, groundwater) [149,152-155]. The analytical limit of detection (LOD) of HPLC–ICP-MS for iodine varies from 4.3 ng I/L to 2 µg I/L, whilst the respective for selenium is 25 ng Se/L – 4 µg Se/L [43,152-158].

In this work, the separation of iodine and selenium species was carried out by anion−exchange chromatography with ICP−MS used as a detector. A more detailed description on the separation conditions is given in Chapter 3.3 and Manuscripts IV and V.

1.5 RESEARCH AIMS

This work aims to obtain information on the site–specific retention of cesium, iodine, niobium and selenium on rather undeveloped Olkiluoto mineral soil and humus, and to gain knowledge on the effect of microbes and abiotic factors on their sorption behaviour. In addition, possible liquid phase species transformations of iodine and selenium caused by the same factors were of research interest. The factors examined in this work included variation in soil depth, time, pH and aeration conditions (aerobic vs. anaerobic), whereas for iodine and selenium also the effect of temperature and microbial activity was investigated. Besides mineral soil and humus samples, the element specific retention was studied on individual soil minerals. This work aimed at:

    I.   To examine the effect of soil depth, time, pH, aeration conditions and OM on the retention of cesium, iodine, niobium and selenium on Olkiluoto soil (Manuscripts I – V)

    II.   To identify the minerals responsible for cesium, iodine, niobium and selenium sorption in Olkiluoto soil and (Manuscripts I, II, IV, V)

    III.   To gain knowledge on the species transformation of iodine and selenium in Olkiluoto soil and to assess the factors affecting them (Manuscripts IV and V)

2 SOIL AND SOIL ENVIRONMENT CHARACTERISTICS AT OLKILUOTO ISLAND

Olkiluoto, an island with a current surface area of about 12 km[2], situates on the coast of the Baltic Sea in south–western Finland (Figure 9). Olkiluoto area belongs to boreal climate regime (Dsc/Dc on Köppen climate classification), and is characterised by mild summer and cool winter [159]. The average annual temperature is approximately 5.9 °C, with observed minimum and maximum temperatures of -27.1 °C and +32.6 °C, respectively, during years 1971–2000 [159]. The annual precipitation is approximately 550 mm.
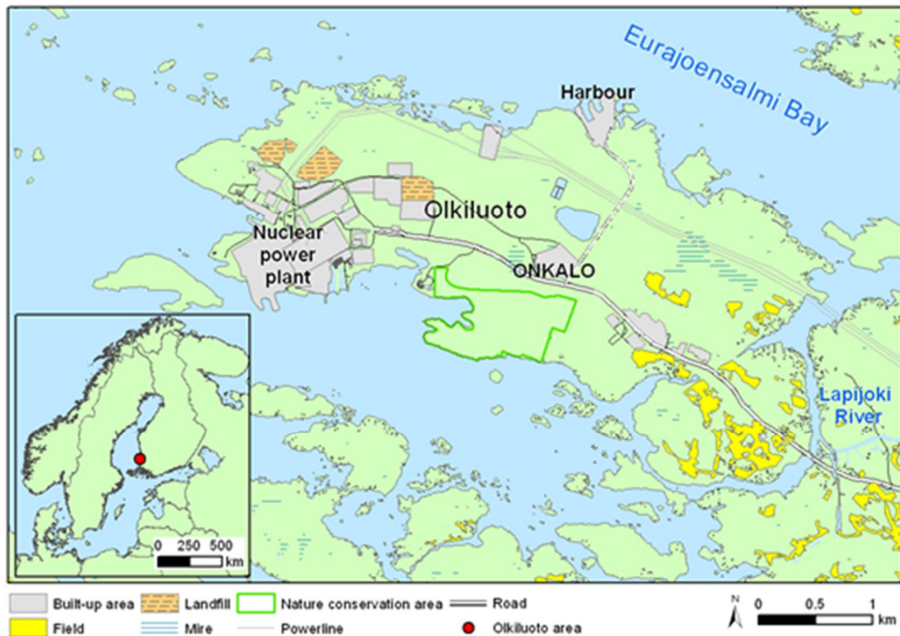
Figure 9. Olkiluoto Island. (Topographic database 2012, National Land Survey, permission 41/MYY/12, layout Posiva Oy/Jani Helin) [164].

Olkiluoto area was covered by a continental ice sheet during the last glacial period causing the crust to sink at the area [159]. After the ice sheet had melted from the top of Olkiluoto area, it was still covered by water for several thousands of years. First glimpses of Olkiluoto area rose above the sea level approximately 2500 – 3000 years ago, and due to the still ongoing post–glacial crustal rebound with a current rate of 6 mm/a, new areas are still emerging [160-162]. The present mean elevation of the area is approximately +5 m

above the sea level, whereas the highest points ascend to +12 − +18 m above the sea level from otherwise flat surface topography [163].

Meadows are the typical primary vegetation cover on the exposed areas and a gradual shift into alder, pine or spruce dominated mesic upland or herb-rich forests typically takes place [16].The most common soil type on Olkiluoto Island is fine-textured till (53 %), followed by sandy till (39 %), gravelly till (4 %), peat (3.4 %) and outcrops (0.6 %) [174]. The thickness of the till cover typically varies from 2 m to 4 m, and the proportion of fine soil particles (Ø < 0.063 mm) and clay particles (Ø < 0.002 mm) is 32 − 41 % and 7 − 14 %, respectively [39,163,165-169]. The typical minerals in order of abundance for gravel, sand and silt fractions (20 mm ≥ Ø ≥ 0.002 mm) are quartz, plagioclase, potassium feldspar, micas, chlorite and hornblende [22,169]. On the other hand, illite, hornblende and chlorite are the typical minerals encountered in the clay fraction (Ø < 0.002 mm) [22,169]. The specific surface area (SSA) of the soil particles varies between 2.3 − 15 m^2/g and density between 2.8 − 3.0 g/cm^3 [168,169].

Overburden at Olkiluoto area was formed during the last glaciation or after that, and is classified as Quaternary deposits [165-169]. Even though soil forming processes started acting immediately after the soil emerged from the sea, Olkiluoto soils are rather undeveloped due to their young age (0–3000 a) and cool and rainy climate conditions [159,170-172]. Soils are most often classified as being Arenosols, poorly developed and immature soil profiles formed in coarse grained soils [172]. In addition to Arenosols, undeveloped Regosols, thin or coarse–grained Leptosols and partly anoxic Gleysols are encountered on Olkiluoto Island. The predominant soil forming process in Finland is natural soil acidification, podzolisation, which causes the leaching of Al and Fe complexed by LMW (low molecular weight) acids (e.g. phenolic, citric and oxalic acids) downwards in a soil profile and their subsequent enrichment upon microbiological breakdown of the LMW carrier [159,171,173]. Podsolization is a slow process as it can take up to 500 − 1500 years for a mature podzol profile to develop on sorted sand soils along the Gulf of Bothnia [170,171]. For this reason, the characteristic leached eluvial and Al+Fe enriched illuvial soil horizons for podzols are not met in the rather undeveloped Olkiluoto soil [168].

In the overburden, OM rich humus layers exhibit higher CECs than the mineral soil layers underneath. Furthermore, soil layers of similar type show variation in their CEC values in accordance with their chemical and mineralogical properties, microbial activity and decomposability of OM [39]. CEC values of 39 − 390 $cmol_{(+)}$/kg has been measured for humus, whilst the range for mineral soil is 8.6 − 62 $cmol_{(+)}$/kg. The main exchangeable cations on the surfaces of Olkiluoto soil particles are Ca^{2+}, Mg^{2+}, K^+, Na^+, Al^{3+} and H^+ [22,39,169]. Base saturation of the soils, i.e. the fraction of Ca^{2+}, Mg^{2+}, K^+, Na^+ cations of soil CEC, shows no systematic behaviour with soil depth. The base saturation for humus varies from 57 % to 99 %, and in mineral soil the range is 52 − 97 % [39]. Dissolved organic carbon (DOC) concentration in Olkiluoto soil solution was the highest in the humus layer, being 124 mg/l, and decreased

systematically with depth averaging to a value of 20 mg/l in the mineral soil [22]. The average concentration of anions present in the soil solution decreased in the order of SO_4^{2-} (63 mg/l) > Cl^- (22 mg/l) > F^- (2.9 mg/l) > NO_3^- (1.0 mg/l), whilst the respective order for major cations was Ca^{2+} (12 mg/l) > K^+ (6.5 mg/l) > Na^+ (5.7 mg/l) > Mg^{2+} (4.9 mg/l) [22]. The average ionic strength of Olkiluoto soil solution is 270 mmol/l [22].

In Olkiluoto soil, OM content systematically decreases with soil depth. The range for OM content in humus was 15.8 – 58.5 mass–%, whilst in mineral soil OM content is typically <1 % [22,39]. SOM has the greatest effect on soil pH conjointly with clay content, but also organic and inorganic acids produced by soil biological activity decrease solution pH [39,175,176]. In Olkiluoto soil, the pH increases systematically with depth from 3.7 – 5.4 in humus to 7 – 8 in mineral soil at depths below 1 m [22,39,163].

Groundwater system in Olkiluoto bedrock is transport–limited, indicating that the water supply from the overburden to the bedrock is higher than the bedrock system can transmit [177]. This is caused by the lower hydraulic conductivity of the bedrock compared with the overburden soils. The hydraulic conductivity of the bedrock is approximately 1.0×10^{-8} m/s, whereas the respective of overburden varies with soil type (range gravel 7.4×10^{-5} m/s – clay 4.5×10^{-7} m/s). The overburden groundwater system is supply–limited, which can result in greater runoff and evapotranspiration with increased precipitation. The average groundwater table in the overburden typically lies approximately 2 meters below the ground surface [39,163,177,178].

On the time scale of geological final disposal of SNF, Olkiluoto surface environment will go through an enormous change [3]. An example of this is the retreat of the coast line due to the crustal rebound and replacement of current sea bottom by terrestrial areas and formation of lakes. Also, the abundance of peatland environments is likely to increase due to overgrowing of shallow water bodies and primary mire formation.

3 EXPERIMENTAL

This section gives the descriptions of the methods of soil sampling and characterisation, summarises the different experimental setups and procedures applied in the determination of distribution coefficient (K_d) values for cesium, iodine, niobium and selenium and gives a general view on the liquid phase speciation analysis of iodine and selenium with the use of HPLC–ICP-MS. More detailed information on soil characterisation, sorption experiments and HPLC–ICP-MS methods can be found from Manuscripts I – V.

3.1 SOIL SAMPLING AND CHARACTERISATION

Aerobic and anaerobic mineral soil samples used in all the Manuscripts except II were collected from a boreal forest soil pit (coded as OL-KK20) excavated on Olkiluoto Island, on the coast of south–western Finland. The soil type was sandy till throughout the pit, which is considered as medium mineral soil in biosphere safety assessment practices in distinction from fine and coarse mineral soil. The coordinates of the soil pit were N 61°13'41.668" and S 21°30'33.735" (EUREF–FIN coordinate system). Five mineral soil depths, namely 0.70 m, 1.30 m, 2.05 m, 3.00 m and 3.40 m, were sampled vertically. Aerobic soil samples were collected with a shovel and preserved in PE–bags, whereas anaerobic samples were taken with a special soil corer (Eijkelkamp 04.16) designed to prevent exposure to air. Anaerobic soil samples were collected on two stainless steel tubes, which were plugged from both ends with PE–caps and secured with duct tape. In addition to mineral soil samples, organic matter rich humus samples were taken from the vicinity of the soil pit with a shovel and preserved in PE–bags. After sampling, aerobic mineral soil and humus samples were transported to laboratory and stored in ambient temperature without any pre–treatment, whilst anaerobic samples were transferred immediately into nitrogen filled glovebox and preserved under nitrogen atmosphere. Aerobic mineral soil samples were sieved into grain size fraction <2.0 mm upon natural drying of the samples. No sieving of humus or anaerobic mineral soil samples was done.

Basic chemical and geotechnical properties were determined for all OL-KK20 soil samples. Soil pH was measured with 1:1 solid to liquid ratio in pure MilliQ water and in 0.01 M $CaCl_2$ solutions. Dry matter content was gained via sample weighing after drying the samples in 105 °C for 24 hours, and organic matter content was determined as loss of ignition at 550 °C. 1 M ammonium acetate solution buffered to a pH value of 4.5 was used for soil cation exchange capacity determination with 1:5 solid to liquid ratio. Weakly crystalline aluminium and iron oxide content was determined by dark extraction with

0.029 M ammonium oxalate and 0.021 M oxalic acid adjusted to pH 3 with 1:25 solid to liquid ratio. Soil mineralogy was determined at Geological Survey of Finland (GTK) with XRD for <0.01 mm and 1.0 – 2.0 mm grain size fractions. The specific surface area of soil and mineral samples were measured at Tampere University of Technology by N_2–BET with FlowSorb instrument and at Chalmers University by Kr–BET with Micromeretics instrument. The results of soil pH, OM content, CEC, weakly crystalline Al and Fe oxide content as well as soil SSA are given in Table 2. Abundancies of soil major and minor minerals for grain size fraction of 1.0 – 2.0 mm can be found in Table 3.

Soil pH increased from 4.6 measured for humus to an average value of 7.1 in mineral soil and was attributed to a concurrent decrease in soil organic matter content with soil depth from 14 % to less than 0.5 %. CEC of humus was relatively low at 13 cmol$_{(+)}$/kg, whereas the lowest and highest CECs of 6.3 cmol$_{(+)}$/kg and 29 cmol$_{(+)}$/kg were observed for the two highest mineral soil layers at the depths of 0.70 m and 1.30 m, respectively. The CEC of all the mineral soil layers averaged to a value of 16 cmol$_{(+)}$/kg. The concentration of soil weakly crystalline aluminium and iron oxides decreased systematically with soil depth from 26 mmol/kg at 0.70 m to 3.5 mmol/kg at 3.40 m. This decrease was simultaneous with a clear drop in soil SSA (Kr–BET) from 4.3 m²/ to 0.38 m²/g at 0.70 m and 3.40 m, respectively.

Table 2. *Chemical and physical characteristics of excavator pit OL-KK20 soil samples (number of samples 2 – 4 from each depth). The values are presented for aerobic soil samples unless otherwise mentioned.*

| Sample type | Soil depth (m) | pH | | | | OM content ± STDEV (%) | CEC ± STDEV (%) | Weakly crystalline Al+Fe oxide content ± STDEV (%) | SSA (m²/g) | |
| | | aerobic | | anaerobic | | | | | | |
		in water ±0.1	in 0.01 M CaCl₂ ± 0.1	in water ±0.1	in 0.01 M CaCl₂ ± 0.1				N₂-BET	Kr-BET ± STDEV (%)
Humus	0.12	5.3	4.6	n. d.	n. d.	14±1	13±3	n. d.	n. d.	n. d.
Mineral	0.70	7.9	7.1	8.6	8.0	0.8±0.3	6.3±2	26±3	6.8	4.3±2
Mineral	1.30	7.8	7.1	9.3	8.5	0.6±0.1	29±1	8.8±1	2.5	1.5±1
Mineral	2.05	7.7	7.1	9.6	8.7	0.5±0.1	19±3	5.8±1	1.4	0.8±1
Mineral	3.00	7.7	6.9	9.5	8.5	0.4±0.1	13±2	3.6±1	1	0.5±1
Mineral	3.40	7.8	6.9	9.6	8.5	0.5±0.1	15±2	3.5±2	0.8	0.4±1

n.d. = not determined

The main mineral at every soil depth was quartz with an average content of 52 % (Table 3), followed by plagioclase (21 %) and potassium feldspar (19 %). The average mica (muscovite) content in the soil samples was <5 % and kaolinite was observed at notably high content of 8 %. Minor minerals hematite and amphibole were detected only in the samples of the grain size fraction <0.01 mm, whereas no swelling clay minerals were observed in any of the samples.

In addition to soil samples, pure individual minerals quartz, potassium feldspar, plagioclase, hornblende, chlorite, hematite, kaolinite, biotite and muscovite were used in the experiments. From these minerals plagioclase was found to be rather impure and contain only 78 % plagioclase ($Na_{0.622}Ca_{0.368}Al_{1.29}Si_{2.71}O_8$) and 8 % potassium feldspar, 4 % chlorite, 4 % magnesite, 3 % quartz and 3 % amphibole as impurity minerals.

Table 3. *The abundance of the main minerals (quartz, plagioclase, potassium feldspar) and minor minerals (kaolinite, mica, amphibole, hematite) of Olkiluoto mineral soil samples from the excavator pit OL-KK20 for the grain size fraction of 1.0 – 2.0 mm.*

Sample depth (m)	Mineral abundance (%)						
	Quartz	Plagioclase	Potassium feldspar	Kaolinite	Mica	Amphibole	Hematite
0.70	60	15	10	10	<5	1–2	<1
1.30	60	25	15	<5	<5	no	no
2.05	50	25	20	5	<5	no	no
3.00	45	20	25	10	<5	<1	<1
3.40	45	20	25	10	<5	no	no

3.2 DETERMINATION OF EXPERIMENTAL K_D VALUES FOR CESIUM, IODINE, NIOBIUM AND SELENIUM

The experimental values of distribution coefficients, K_d, were investigated in batch sorption tests with humus and mineral soil. The liquid phase used in the experiments was synthetic model soil solution (MSS) (Table 4), which represents the measured Olkiluoto soil solution composition. In batch experiments, 1.00 g of soil was weighted into a 50 ml PP–centrifuge tube and 25 ml of synthetic model soil solution was added. In the distribution coefficient experiments for cesium and niobium radioactive tracers $^{134}Cs^+$ and $^{95}Nb(OH)_5$ were used and were added to the samples at 2.3×10^{-8} M and 3.2×10^{-13} M concentration levels, respectively. For iodine and selenium stable elements were used and they were added in the initial chemical forms of iodide (I^-) or iodate (IO_3^-) and selenite (SeO_3^{2-}) or selenate (SeO_4^{2-}). The concentration of iodide, iodate and selenite in the samples was 7.9×10^{-7} M, whereas the respective of selenate was 7.0×10^{-7} M. All sorption samples were prepared in duplicate, except for humus in iodine experiments. Additional background samples containing only MSS and soil were done in iodine and selenium experiment series and treated similarly with the sorption samples.

Table 4. *The chemical composition (mg/l, mmol/l) of the synthetic Olkiluoto model soil solution as based on the concentration measurements of the main elements of Olkiluoto soil solution.* [16,179]

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

The samples were equilibrated for a selected time period typically ranging from one to 49 days but even periods of 63 and 245 days were applied. The incubation was done with a reciprocal shaker allowing the continuous mixing of the liquid and solid phases due to the rotating movement of the shaker, or in sample racks on laboratory table demanding daily manual shaking of the samples to ensure the phase mixing. After the selected time periods, the samples were centrifuged for 10 minutes at 48 400 *g* and syringe filtered through a 0.20 μm Supor® filter. The final activity of radioactive [134]Cs and [95]Nb tracers was measured by gamma spectrometry with sodium iodide detector (Wizard™ 3") and the experimental values of distribution coefficients were calculated from Equation 1. The concentrations of stable iodine (iodide or iodate) and selenium (selenite and selenate) were quantified with HPLC–ICP-MS from the filtrates. The K_d values for selenium species and iodide were calculated from Equation 1, whereas Equation 2 was applied for iodate to correct the solid phase concentration by the reduced iodate fraction (i.e I^-). The presentation of K_d values throughout the text is in the form of (K_d) value ± STDEV of parallel samples, except for iodine humus K_d value, for which the error is based on concentration measurement uncertainty. Solution pH was recorded from the activity measurement samples ([134]Cs, [95]Nb) or prior the phase separation (I, Se).

(1) $$K_d = \frac{c_i - c_f}{c_f} \times \frac{V(ml)}{m(g)}$$

where C_i is the initial concentration and C_f is the final concentration of cesium, iodide, niobium, selenite or selenate in the solution, *V* is the solution volume (ml) and *m* is the sample dry mass (g).

(2) $$K_{d\ IO_3^-} = \frac{\left(c_{IO_3^-\ i} - c_{IO_3^-\ f}\right) - c_{I^-\ f}}{c_{IO_3^-\ f}} \times \frac{V\ (ml)}{m\ (g)}$$

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

To investigate the effect of anaerobic soil conditions on the retention of elements on soil, additional experiments with cesium, iodine and selenium were conducted in a glovebox under oxygen deficient nitrogen atmosphere. In

these tests 0.5 – 5 g of soil was added to the centrifuge tubes, followed by introduction of 25 ml of MSS and tracer. Both MSS and the tracer solution were equilibrated with the nitrogen atmosphere prior the addition. The tracer concentration used in anaerobic batch tests was equal to the ones given for aerobic batch tests. In iodine and selenium experiment series additional background samples were done and treated similarly to the sorption samples. All the samples were kept in sample racks from one to maximum of 49 days and shaken daily to ensure the mixing of the liquid and solid phases. After the selected time period, solution E_h and pH were recorded and the phases were separated by sedimentation and syringe filtration through a 0.20 µm Supor® filter (iodine and selenium), or centrifugation and syringe filtration (cesium). Cesium activity measurement with Wizard™ 3" required a 10 ml aliquot of filtrate, whereas 1 ml was sufficient volume for iodine and selenium concentration analysis with HPLC–ICP-MS. Soil mass weighing, centrifugation and concentration measurements were done outside the glovebox, whereas the other stages were performed within the box. The O_2 level varied with time and working stage, but remained under 20 ppm throughout the studies. The CO_2 level was unchanged at 23 ppm.

Solution pH has a marked effect on the retention tendency of elements through the protonation and deprotonation of surface hydroxyl groups and possible speciation changes. Due to this, experiment series with solution pH adjustment to a desired value in pH range of 4 – 9 prior to tracer introduction were executed by the addition of 0.1 M HCl or 0.1 M NaOH. The experiments were conducted both in aerobic and anaerobic conditions with the soil sample from the depth of 0.70 m. One week incubation time was applied. Otherwise the setup followed the scheme described for aerobic and anaerobic batch tests.

Temperature may bear a significant importance in the sorption of iodine and selenium. Thus, similar experiments as described for aerobic tests were conducted with the exception that the temperature was controlled at +8 °C, +22 °C or +38 °C. Aerobic soil sample from the depth of 0.70 m and seven days incubation time was used. Additional tests were done for speciation analysis of iodine and selenium by keeping soil samples at -22 °C for six days and letting them thaw for overnight at laboratory table in room temperature.

In multiple investigations soil microbes have been elucidated to have a positive effect on the retention and speciation of elements in soil. To verify the role of soil microbes in the sorption of iodine and selenium, microbe–free samples were prepared by weighing 1.00 g of <2.0 mm sieved mineral soil from sample depth 0.70 mm into a 50 ml PP–centrifuge tube and by thrice sterilising them in an autoclave at 120 °C for 20 minutes at a time. The difference between the two first sterilisations was one week, whereas for the two last sterilisations three days intermission was applied. MSS, iodine and selenium solutions were filtered through thrice ethanol washed 0.20 µm filter before introduction into the samples. The samples were incubated for seven days before phase separation and concentration measurements.

Sample mineralogy is known to bear a considerable effect on the retention of elements on soil. Therefore, sorption experiments with individual mineral phases quartz, potassium feldspar, plagioclase, hornblende, chlorite, hematite, muscovite and biotite were done in order to assess their retentive properties and significance in Olkiluoto soil retention of the studied elements. For the experiments, the minerals were crushed and sieved into a grain size fraction of 0.075 – 0.30 mm. Then 0.20 g of each mineral was weighed into a 20 ml PE–scintillation bottle and 20 ml of MSS was added. For niobium additional tests were conducted using calcium free MSS in order to assess the effect of Ca^{2+} on the sorption of niobium at elevated pH values. Solution pH was adjusted to a pH value of approximately 8 before the tracer addition by 0.1 M HCl or 0.1 M NaOH. After the pH was stabilised, radioactive tracer [134]Cs or stable elements niobium ($(NH_4)_3[NbO(C_2H_4)_3]$, Nb concentration 4×10^{-6} M), iodine (iodide or iodate) or selenium (selenite or selenate) were introduced. For iodine and selenium additional background samples consisting of just the mineral and MSS were prepared and treated similarly to the sorption samples. Seven days incubation time in reciprocal shaker was applied, followed by pH measurement and phase separation by filtration through a 0.20 mm Supor® syringe filter. Final [134]Cs activity was measured with Wizard™ 3", concentration of niobium with ICP-MS and those of iodine and selenium with the use of HPLC–ICP-MS. K_d values were calculated from Equation 1 for all elements and species except for iodate, for which Equation 2 was used.

3.3   DETERMINATION OF EXPERIMENTAL LIQUID PHASE SPECIATION OF IODINE AND SELENIUM

Iodine and selenium speciation from the liquid phase of the respective sorption samples was investigated by the use of HPLC–ICP-MS equipped with Dionex AS11 anion exchange column (i.d. 4 × 250 mm, bead Ø 13 µm, pore size <10 Å) and Dionex AG11 (i.d. 4 × 50 mm) guard column. In the liquid phase speciation analysis of both elements and their anionic species, isocratic eluent flow with a flow rate of 0.8 ml/min and constant introduction of internal standard [45]Rh to the eluent flow through a T–junction inserted between the separation column and ICP-MS nebulizer was applied. The eluent in iodine analysis was 15 mM NaOH, whereas 10 mM NaOH was applied for selenium. The eluent was bubbled with argon gas throughout the measurements to remove any traces of dissolved CO_2.

The total measurement time for anionic iodine moieties was 900 s; iodate was detected at 125 ± 1.7 s and iodide at 598 ± 55 s (Figure 10). The LOD value of iodate with 10σ criterion was 0.30 µg/l and for iodide 1.51 µg/l. Reagent blanks and a combined iodate and iodide standard containing 5 µg/l of both species was measured as a part of the HPLC–ICP-MS stability verification. The standard measurement yielded 4.81 ± 1.08 (STDEV) µg/l for iodate and 4.61

± 1.93 µg/l for iodide. Per centual reduction of iodate to iodide observed in some samples was calculated from Equation 3. The reduction percentages are presented in the form of value ± STDEV of parallel samples throughout the text, except for iodate in humus, for which the error is based on concentration measurement uncertainty.

$$(3) \qquad reduction\ \% = \frac{c_{I^- \, f} \; - \; c_{I^- \, bkg}}{c_{I \, i}} \times 100\ \%$$

where $c_{I^- \, f}$ is the final concentration of iodide in the solution, $c_{I^- \, bkg}$ is the iodide concentration in the background samples (i.e. extracted from the soil) and $c_{I \, i}$ is the iodine concentration added to the samples in the beginning of the experiments.
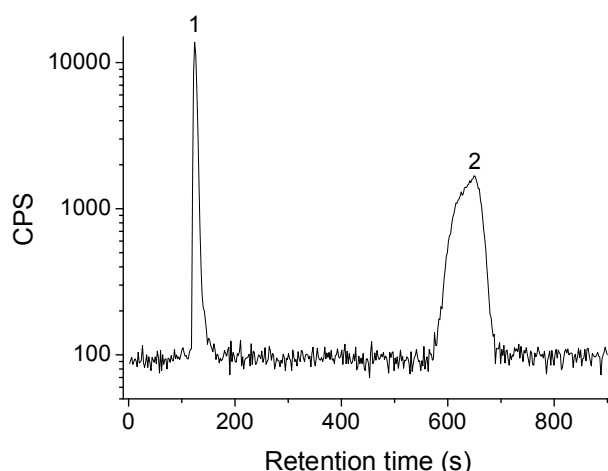

Figure 10. Iodine HPLC–ICP-MS chromatogram of a mixture of iodate (1) and iodide (2) standards at 25 µg I/l concentration level for both species.

The total measurement time for each sample in selenium speciation analysis method was 480 s. Selenite peak was detected at 227 ± 15 s and selenate at 355 ± 20 s (Figure 11). The LOD values for anionic selenium species selenite and selenate were 0.86 µg/l and 0.74 µg/l, respectively. The measurement of a combined selenite and selenate standard at 5 µg/l of both species yielded 5.24 ± 1.08 µg/l for selenite and 5.25 ± 1.46 µg/l for selenate. In addition to concentration standard, reagent blanks were measured at certain intervals to ensure the ICP-MS stability.
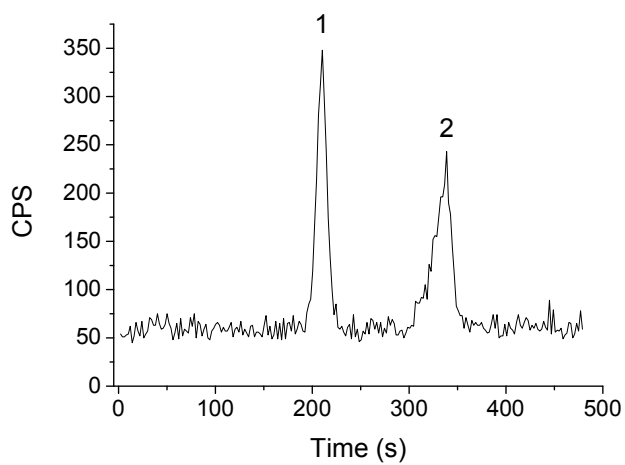
Figure 11. Selenium HPLC–ICP-MS chromatogram of a mixture of SeO_3^{2-} (1) and SeO_4^{2-} (2) standards at 5 µg/l concentration level for both species.

4 RESULTS AND DISCUSSION

In this Chapter the results of cesium, iodine, niobium and selenium sorption on humus, mineral soil and minerals as well as liquid phase speciation changes of iodine and selenium in the experimental conditions are covered and discussed. More elaborate presentation can be found from Manuscripts I – V.

4.1 SORPTION

Sorption is a general term describing the tendency of an analyte to adhere to solid phase and sorption experiments are conducted to evaluate this strength. Sorption is typically dependent on different factors, such as solution pH and composition and solid phase mineralogy. Thus, sorption experiments of cesium, iodine, niobium and selenium on Olkiluoto mineral soil were varied according to e.g. incubation time, soil depth, aeration conditions and pH. Additional tests were done with humus and individual mineral phases (e.g. quartz, potassium feldspar, plagioclase, hematite, and muscovite) encountered in Olkiluoto soil in varying proportions.

4.1.1 EFFECT OF TIME (MANUSCRIPTS I, III – V)

Incubation time had a clear sorption increasing effect for cesium (Figure 12 A), selenite (Figure 12 C), iodide and iodate in aerobic soil conditions. In the following examples, the K_d values presented for cesium, iodine, niobium and selenium are for 0.70 m mineral soil sample. The retention of cesium increased from 3400 ± 30 ml/g at day 1 to 8300 ± 400 ml/g at day 21 corresponding a 2.4–fold increase. At a time range from 1 to 49 days, the K_d values of iodide and iodate increased 5–fold (from 1.0 ± 0.3 ml/g to 4.8 ± 0.5 ml/g) and 3–fold (from 2.1 ± 0.4 ml/g to 7.4 ± 1.3 ml/g), respectively, whilst the respective increase for selenite was 6–fold (from 26 ± 2 ml/g to 170 ± 2 ml/g). Selenate retention tended to decrease with increasing incubation time, e.g. from 4.1 ± 0.1 ml/g at day 1 to 1.1 ± 0.4 ml/g at day 49.

For niobium (Figure 12 B), time was not an important factor since an apparent sorption equilibrium was reached with the shortest 7–day incubation period applied, and further increase from 7 to 63 days promoted only moderately higher sorption. For example, the [95]Nb K_d value for 0.70 m sampling depth at 7 and 63 days incubation times were 180 000 ± 4000 ml/g and 310 000 ± 14 000 ml/g for filtered samples, respectively. In the experiments, [95]Nb was found to be strongly associated with soil–originated colloidal material. Colloids having diameter larger than 0.20 μm were removed by filtering, and on average, this caused [95]Nb activity to decrease by 44 – 71 % in the samples.

Increase in the retention with time is generally proposed to be caused by initial fast uptake e.g. by outer sphere complexation followed by slow diffusion on the less available sites which for cesium include those within the particles and interlayer spaces (i.e. FES sites) of clay and mica minerals [23,116,180,181]. For iodine, the slow process is e.g. molecular diffusion into the inner spaces of soil particles and retention within [56,134]. For selenite, fast initial immobilization is suspected to be followed by phase transition into less labile ones e.g. by complex formation between selenite and dissolved OM, stronger binding of selenite from initial outer sphere complex to a form of inner sphere complex non–exchangeable with phosphate or diffusion into more access–limited internal sites [87,182,183]. In general, time tends to affect the retention of elements in such a way that they redistribute to soil phases among which the elements will present greater stability and less reactivity [182].
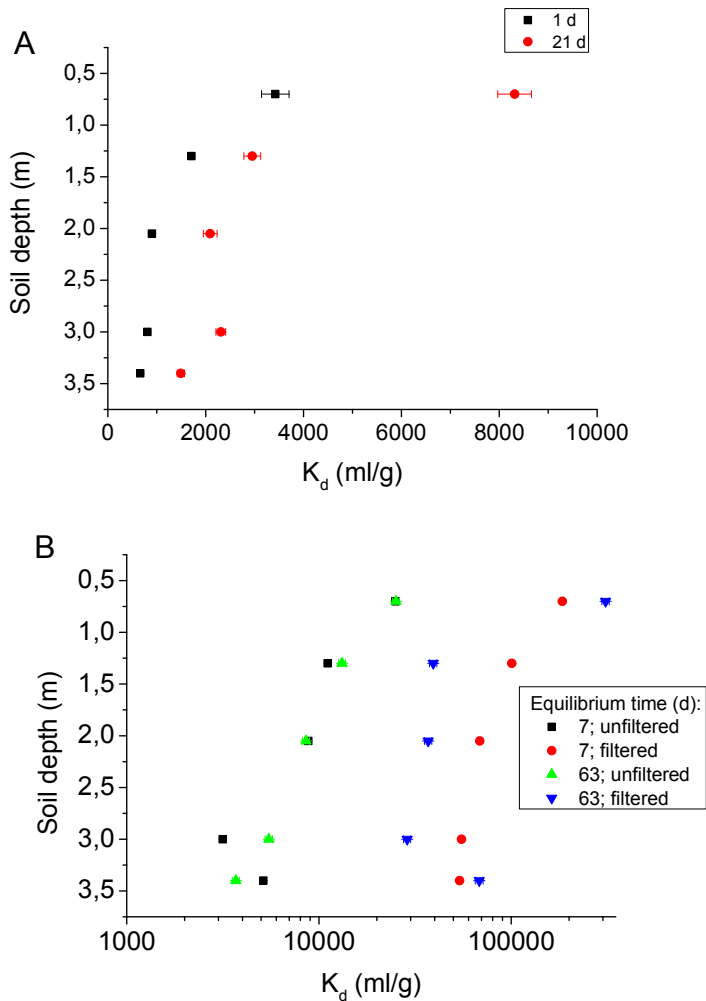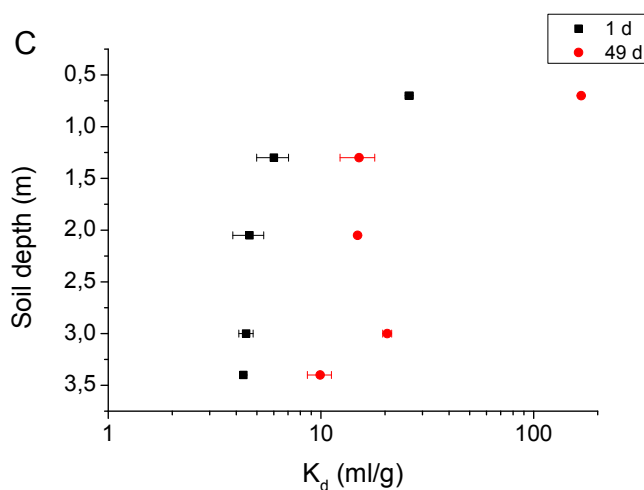
Figure 12. The K_d values of cesium (A), niobium (B) and selenium (selenite) (C) on aerobic Olkiluoto mineral soil at different equilibrium times.

4.1.2 EFFECT OF SOIL DEPTH (MANUSCRIPTS I, III – V)

Soil depth presented a clear, decreasing effect on the retention of cesium and niobium (Figures 12 A and 12 B). The average K_d value of ^{134}Cs decreased from 5 500 ± 1 600 ml/g at 0.70 m to 1 300 ± 700 ml/g at 3.40 m in aerobic soil conditions. For ^{95}Nb, the average K_d value of 150 000 ± 7 000 ml/g at 0.70 m decreased to 39 000 ± 2 000 ml/g at 3.40 m for samples filtered to remove colloidal–bound niobium. A slight decrease in iodate sorption with soil depth was observed, as the average K_d value decreased from 3.6 ± 1.9 ml/g at 0.70 m to 1.3 ± 0.7 ml/g at 3.4 m. Selenite showed approximately 4 – 6 times higher retention on the samples of the highest sampling depth at 0.70 m than on the other mineral soil samples (1.3–3.4 m) in aerobic conditions. The K_d value of selenite at 0.70 m ranged from 26 ± 2 ml/g to 240 ± 40 ml/g, as for the depths of 1.3 – 3.4 m the K_d value showed only a slight variation and averaged to a value of 6.2 ± 4.7 ml/g. Quite surprisingly, selenate exhibited opposite behaviour with soil depth than cesium, niobium or iodate, as the average K_d values increased from 2.1 ± 1.5 ml/g at 0.70 m to 10 ± 19 ml/g at 3.40 m. Iodide was the only studied species that had no clear dependence on soil depth.

The decrease in the sorption of cesium and niobium with soil depth was attributed to the same variables for both, namely decrease in soil CEC, SSA and possibly in clay fraction content. However, CEC and SSA can presumed to be indicators of soil clay fraction content [184] since clays and clay fractions form the backbone of both variables [185,186]. Cesium exhibited high positive correlation coefficient of +0.993 between the average K_d values (0.7 – 3.4 m) and SSA, whilst the correlation between the average K_d values of sample depths 1.3 – 3.4 m and CEC was only moderate at +0.693. The respective values for niobium were +0.979 and +0.876. Sample depth 0.7 m was an

exception in the correlation calculations between the K_d value and CEC as caused by its low CEC of 6.3 cmol$_{(+)}$/kg and good retentive properties. Also, niobium exhibited high negative correlation with pH (-0.630), whereas cesium had no correlation (+0.059). The negative correlation is indicative of decreasing sorption with increasing pH. However, a strong positive correlation of +0.988 between average K_d value of niobium and soil weakly crystalline Al+Fe oxide content can give support to the expected sorption mechanism of niobium (inner sphere complexation), and also on the importance of these soil components on niobium soil retention.

For selenite, the retention was attributed to the variation in soil SSA (+0.968), weakly crystalline Al+Fe oxide content (+0.977), OM content (+0.926) and soil pH (-0.943). These correlations are logical as OM is an important sorbent for selenium in soils [99,100,130] and soil weakly crystalline Al and Fe oxides serve as sorbents for selenite mainly through inner sphere complexation [97,105]. However, Al and Fe bearing phases can be highly important even when mingled within the OM matrix [100]. Increase in solution pH affects the surfaces of soil particles by increasing the fraction of deprotonated surface functional groups (M−O$^-$) thus reducing the fraction of exchangeable ligands (M−OH$_2{}^+$ and M−OH groups), and also by inducing a change in the dominant selenium species from HSeO$_3{}^-$ to SeO$_3{}^{2-}$ (at about pH 8.4) [21,44]. As negative surface charge repels anionic selenite form its vicinity and the tendency for inner sphere complexation decreases in the absence of exchangeable ligands, the findings on decreasing selenite sorption with increasing pH are logical [98,102,132,133,135]. The observation of the pH of sample depth 0.7 m being systematically lower than the respective of the depths of 1.3 − 3.4 m, the average pH values corresponding to 7.6 ± 0.6 and 8.8 ± 0.4, gives further support to this observation. The correlation between selenite average K_d values and soil SSA is expected as SSA is partly induced by soil weakly crystalline Al+Fe oxides [187].

The non−existent sorption dependence of iodide, iodate and selenate with soil depth does not necessary correspond reality, but can be caused by their low sorption as partly induced by their relatively high initial concentration in the liquid phase (I$^-$ and IO$_3{}^-$ 7.9 × 10^{-7} M, SeO$_4{}^{2-}$ 7.0 × 10^{-7} M). The correlations between the average K_d values of selenate or iodide and OM content, CEC, SSA and weakly crystalline Al and Fe oxide content were all non−existing (iodide) or weak (selenite). In spite of the absence of a clear systematic sorption behaviour of iodate with soil depth, a negative correlation between the average K_d value and pH (-0.605) and positive correlation between average K_d and OM content (+0.456), SSA (+0.486) and weakly crystalline Al+Fe oxide content (+0.490) was observed. The presence of these correlations are expected and for pH and weakly crystalline Al+Fe oxides caused by the same reasons as discussed for selenite [21,38,56,188 128,141]. Organic matter is known to be the major sorbent for iodine species in soils because of the variety of functional groups participating in the sorption reactions on a wide range of pH values from acidic to basic [21,36-38,56,134] and its presence can lead iodine speciation changes

through formation of OM−I compounds exhibiting stronger affinity towards mineral phases than inorganic iodate form [43,47,48,51,52,57,58,189].

4.1.3   EFFECT OF AERATION CONDITIONS (MANUSRIPTS III – V)

Figure 13 presents the K_d values of cesium (13 A), selenite (13 B) and selenate (13 C) on Olkiluoto soil in aerobic and anaerobic conditions. Cesium was retained slightly better in aerobic soil conditions than in anaerobic ones, as depicted on average 1.5–times higher K_d values determined for aerobic soil. As an example of the retention, the average K_d value of ^{134}Cs for sample depth 3.4 m increased from 650 ± 160 ml/g to 1300 ± 700 ml/g upon soil reduction status changing from reductive (average E_h -2.3 mV) to oxidative (average E_h +460 mV). Selenate presented on average 4–times higher K_d values in aerobic soil compared with anaerobic soil (average E_h +150 mV).

Iodide and iodate were retained slightly better in aerobic soil conditions than in anaerobic ones as indicated on average by 1.3– and 2.5–times lower K_d values for iodide and iodate, respectively, on anaerobic soil. The average K_d values for both species were below 4 ml/g in aerobic and anaerobic soil conditions, whereas the average E_h value for iodide samples was +170 mV and for iodate +120 mV. For selenite, the highest sampling depth 0.7 m showed clearly higher retention in aerobic soil than in anaerobic, as the K_d values were on average 11–times higher in aerobic soil. For soil depths 1.3 – 3.4 m selenite K_d values were comparable between the aeration conditions. The redox potential of selenite samples from the depth of 0.7 m averaged to +260 mV whereas the respective value for sample depths 1.3 – 3.4 m was +160 mV.

Change in soil redox potential can have a marked effect on the retention of elements either directly through changes in element speciation or indirectly e.g. by changes in soil solution or solid phase composition. Since cesium is not a redox sensitive element and in the experimental conditions it is present solely as hydrated Cs^+ cations, the decreasing redox potential must affect cesium retention by other means. A plausible, but not experimentally verified mechanism, is the formation of NH_4^+ ions [116]. These ions are known be to highly competitive on the FES sites present in certain clay and mica minerals [23,110] and to liberate sorbed cesium from ion exchange sites [190]. The formation of NH_4^+ ions has been observed to increase considerably upon formation of reducing soil conditions [116], and the hypothetical E_h limit for NO_3^- reduction into NH_4^+ ions in pH 8 lies at < +300 mV [19].

Slightly lower retention of iodine in anaerobic conditions versus aerobic ones is presumed to be caused by desorption of iodide from soil surfaces and reduction of iodate into iodide [47,153,191,192]. In liquid phase speciation studies of the anaerobic samples an observation on the increased iodate reduction into iodide with increased incubation times was obtained: the reduced iodate fraction increased from 0 % on day one to 55 % on day 49 (see Chapter 4.2.1).

As selenium is one of the redox sensitive elements typically presenting higher retention upon decreasing redox potential and formation of reduced

selenium species, the slightly higher retention of selenate in aerobic conditions was surprising. However, the K_d values determined in anaerobic and aerobic conditions were very low, being < 5 ml/g in general, which in turn makes it difficult to notice any difference in its sorption behaviour. One of the reasons for the lower sorption in anaerobic soil conditions can be that indications on the reduction of selenate to selenite was not observed (or SeO_3^{2-} quantity was below the LOD of HPLC–ICP-MS method), probably caused by the rather high E_h of +150 mV and pH of 9.4. Also, the slightly lower average pH for aerobic samples (8.6) would, in turn, indicate slightly more positive surface for selenate to be electrostatically attracted to and thus explain the higher sorption. An exhaustive explanation for the higher retention of selenite on 0.7 m samples in aerobic conditions versus anaerobic ones is not available. For sampling depths 1.3 – 3.4 m the retention was rather comparable between both incubation conditions, and it is presumed that the sorption was more affected by pH (average of 8.8 ± 0.4 aerobic, 9.5 ± 0.1 anaerobic) than the soil redox potential. Liberation of sorbed selenate and selenite from soil weakly crystalline Fe oxides upon reductive dissolution is not likely to occur due to the high measured E_h value of the samples (+150 mv … +260 mV) in comparison with the values for Fe(III) reduction (+80 mV … +110 mV) [107].
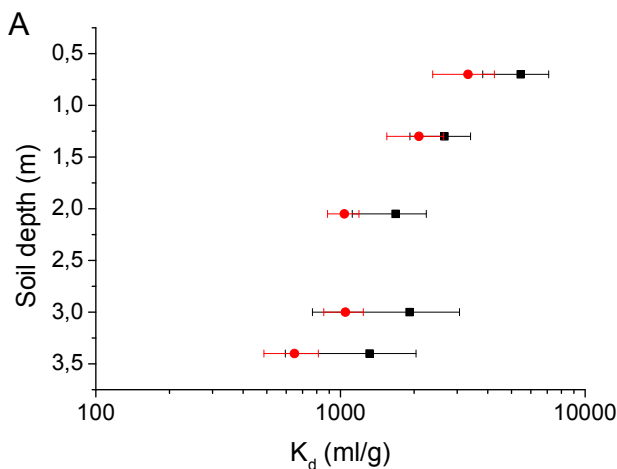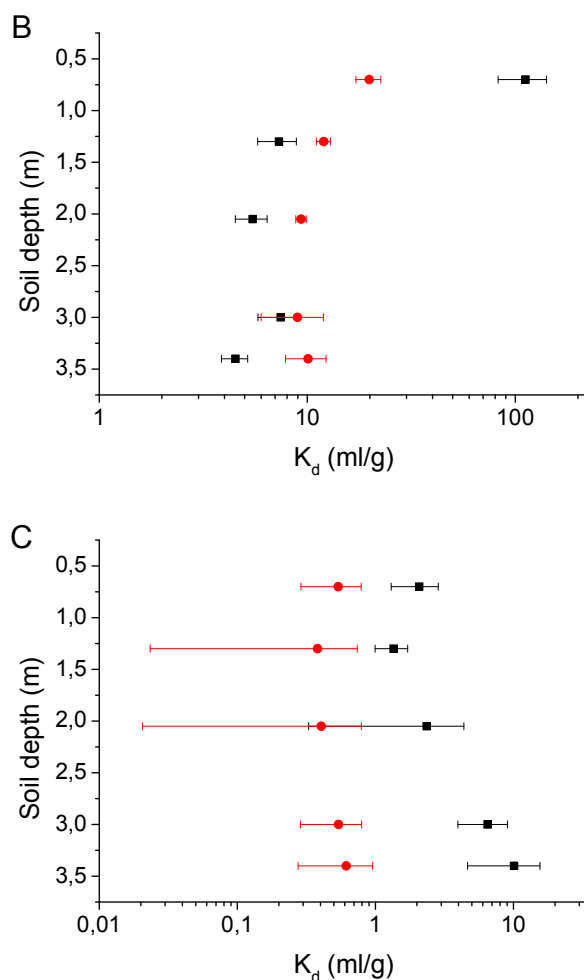
Figure 13. The average K_d values of cesium (A), selenite (B) and selenate (C) for aerobic (square) and anaerobic (circle) Olkiluoto soil samples.

4.1.4   EFFECT OF HUMUS (MANUSCRIPTS I, IV,V AND UNPUBLISHED DATA)

The typical assumption of soil organic matter being the dominant sorbent for anions in soil proved to persist only for iodide and iodate. For these species, the K_d values for humus were approximately 4–fold and 20–fold, respectively, than for aerobic mineral soil from the depth of 0.70 m with the same applied incubation times (1 – 21 days). For humus and aerobic mineral soil the average K_d values of iodide were 8.8 ± 15 ml/g and 1.4 ± 1.2 ml/g, whilst the respective values for iodate were 53 ± 79 ml/g and 2.3 ± 0.5 ml/g. The retention of iodate showed systematic increase with time, whereas no such behaviour was observed for iodide.

The retention of cesium, niobium and selenite was lower on humus than on aerobic mineral soil from the depth of 0.70 m. For cesium, the K_d value for humus decreased with time from 6600 ± 500 ml/g on day 7 to 1800 ± 200 ml/g on day 23, and averaged to a value of $4000 \pm 2\,000$ ml/g. The respective average for aerobic mineral soil from the depth of 0.7 m was 5400 ± 1600 ml/g indicating 1.4–times lower average cesium retention on humus than on the topmost mineral soil layer. Aerobic mineral soil retained niobium far more better than humus, as the difference in the ^{95}Nb K_d values between the soil types was over 160–fold. The highest niobium K_d value determined for humus was 810 ± 3 ml/g, whereas for mineral soil K_d value as high as 185 000 ml/g was obtained. Quite oppositely to iodate, the retention of niobium on humus tended to decrease with increasing incubation time, only to approximately reach the initial K_d value on the longest incubation period of 28 days. In humus, a smaller fraction of niobium was retained on colloids than in mineral soil, as solution filtration induced a decrease in ^{95}Nb solution activity only by 3 – 11 % in comparison with 44 – 71 % for mineral soil. For selenite, the retention on aerobic mineral soil from the depth of 0.7 m was approximately 3–times higher than on humus as the average K_d values were 112 ± 78 ml/g and 32 ± 25 ml/g. No retention of selenate was detected on humus at any of the studied incubation times. Niobium (14 A) and selenite (14 B) retention on Olkiluoto humus as a function of incubation time is presented in Figure 14.
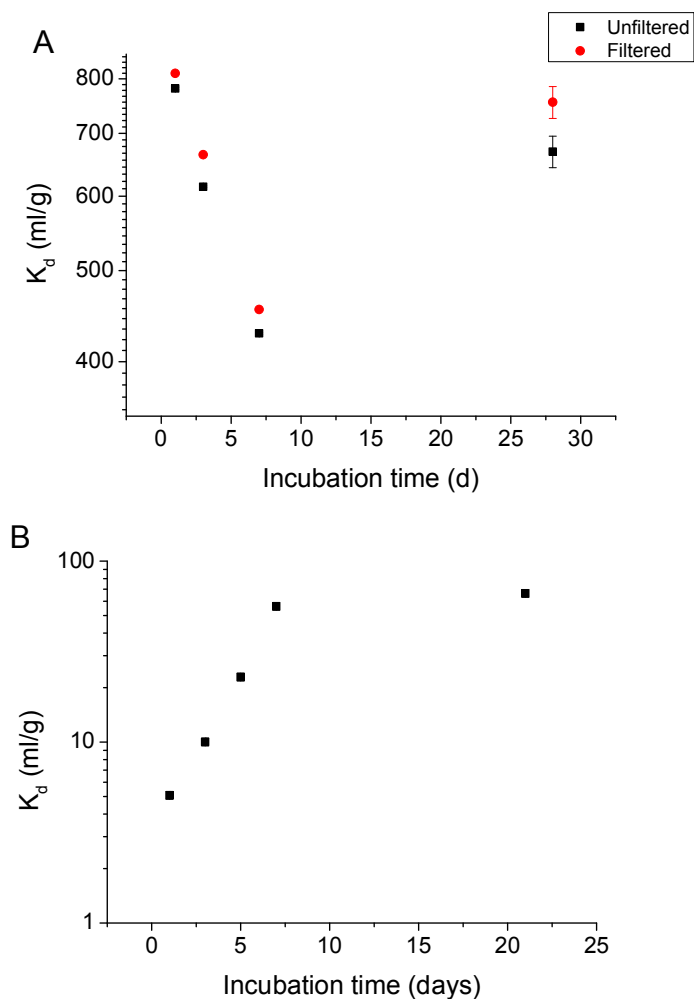
Figure 14. The K_d values of niobium (A) and selenium (selenite) (B) on organic matter rich humus as a function of incubation time.

Organic matter is considered as a poor sorbent for cesium due to its weak retention on non–specific ion exchange sites tending to remain in their protonated or neutral form in the experimental and environmentally encountered pH values (3.7 – 5.4 in Olkiluoto humus), and thus expel positively charged cesium from their immediate proximity [10,21,103,119,120]. It has been proposed that FES sites on certain clay and mica minerals account for cesium retention in OM rich soil layers [120-122], but these sites are prone to steric hindrance arising from retention of organic macromolecules on Al–OH sites situating in the vicinity of the FES sites [21,123,124]. However, in Olkiluoto soil it is evident that OM is not an efficient sorbent for cesium, but the main retention takes place on the inorganic soil minerals possibly also within the OM matrix.

OM is known to be an important sink for selenium and iodine in soil due to the multiplicity of functional groups present [21,36-38,56,99,130,134,135]. OM, and microbial activity within, can cause iodine and selenium speciation to change from inorganic I^-, IO_3^-, SeO_3^{2-} and SeO_4^{2-} forms by the microbial assimilation of iodine or selenium on OM and subsequent formation of OM−I and OM−Se species with varying properties [43,47,48,51,52,57,58,81,154,189,193]. In liquid phase speciation studies the formation of unidentified, presumed OM−I compounds were observed for humus samples, whereas no indication on the formation of OM−Se compounds was received. However, OM−I compounds are found to present higher affinity towards soil than inorganic forms of iodine, and even comprise the main fraction of iodine retained by mineral phases [42,43,58,189]. A conclusion on the experimental results is that in Olkiluoto soil weakly crystalline Al+Fe oxides are very important components for selenium soil retention and OM plays a minor role. On the contrary, OM is the main sorbent for iodine in Olkiluoto soil and iodine enrichment can be expected in places with high OM content. The low retention of niobium on humus indicates OM being rather insignificant for niobium soil sorption and the main enrichment to occur in soil mineral compartment.

4.1.5 EFFECT OF PH (MANUSCRIPTS I, III – V)

The effect of pH on the retention of cesium, iodide and iodate, niobium, selenite and selenate was investigated by adjusting MSS pH to a desired value in the range of 4 − 9. Figure 15 presents the K_d values of cesium (15 A), iodide and iodate (15 B), niobium (15 C) and selenite (15 D) as a function of solution pH. Overwhelmingly lowest retention was shown by selenate, which was not retained at any of the studied pH values. Among the studied elements, niobium was retained the best and it exhibited a sorption plateau of approximately 29 000 ± 3 000 ml/g at pH of 3.5 − 6.5, after which its retention decreased to a value of 2700 ± 100 ml/g at pH 9.6. The retention of selenite, iodide and iodate decreased systematically with increasing pH. For selenite, a 10−fold decrease in the K_d value was observed with pH increasing from 4.3 to 8.9, whereas for iodide and iodate the decrease was approximately 5−fold. Cesium retention showed opposite behaviour to anions, as its K_d value increased with pH from 670 ± 13 ml/g at pH 4.2 to over 2000 ± 300 ml/g at pH 9.4.
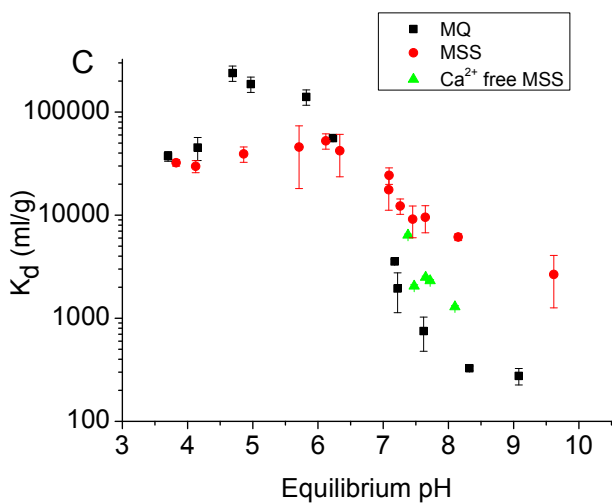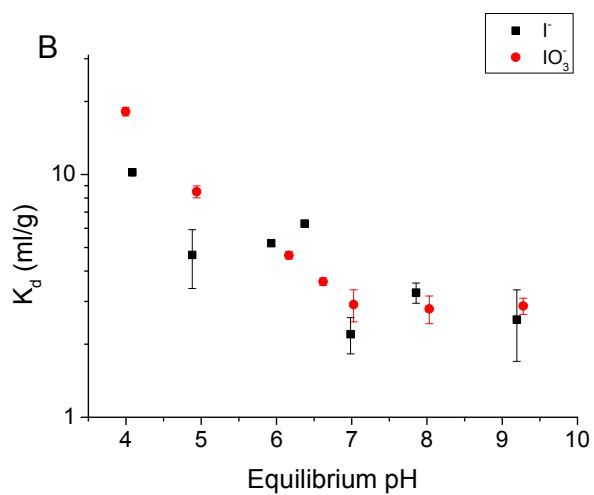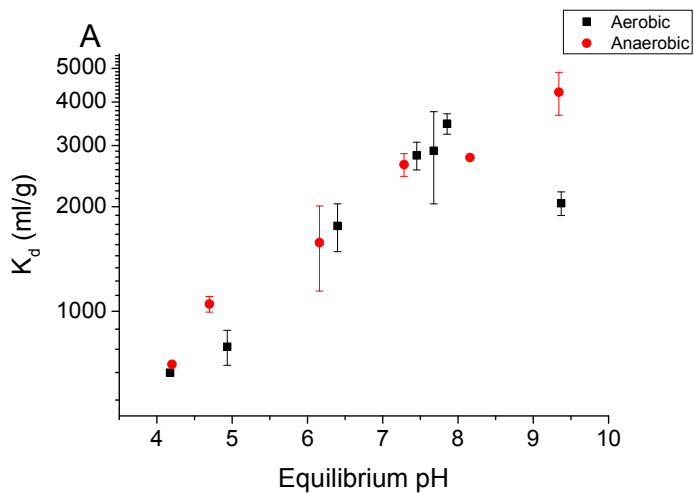
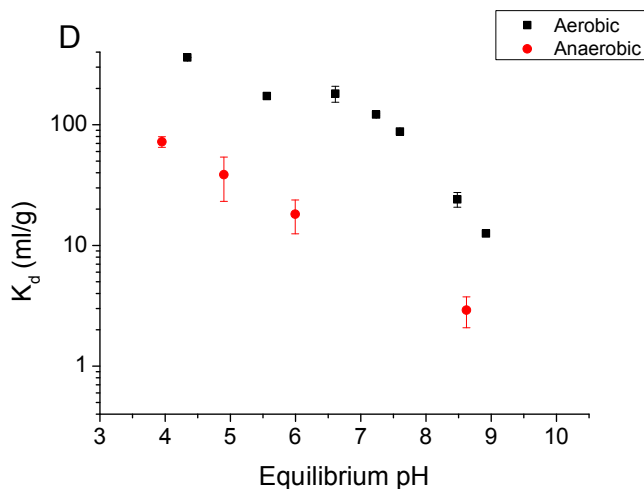**Figure 15.** The K_d values of cesium (A), iodine (B), niobium (C) and selenium (selenite) (D) as a function of solution equilibrium pH.

Solution pH is known to affect the retention of elements on soil. Typically this effect is through the protonation and deprotonation of surface functional groups, such as M−OH (M = central metal cation, e.g. Al, Fe, Mn, Mg, Si). In the case of anions, the most important groups are the hydroxyls of aluminium and iron, Al−OH and Fe−OH groups. These groups represent relatively high pK_a value of approximately $8 - 9$, which indicates that they retain their basic character (i.e. protonated form) even in slightly alkaline solutions. Decrease in the pH tends to favour retention of anions by the increase in the fraction of positively charged protonated (M−OH$_2^+$) surface functional groups [21,38,56,60,98,132,133,194]. This is the reason why the maximum retention of iodine and selenium has been observed to take place at slightly acidic conditions of pH < 4 [31,56,60,98,102,132,133,135,136,188,194]. Similarly, increase in the pH induces the fraction of negatively charged deprotonated functional groups to increase (M−O$^-$), and retention of cations is favoured [29,195]. These trends were also detected here as higher sorption of anionic iodide, iodate and selenite in acidic pH values and increased retention of cationic cesium in elevated pH values. Niobium showed a similar trend as other anions, but its retention remained at a rather high level even in elevated pH values.

For iodine, niobium and selenium, pH affects also their speciation and proton association reactions. For iodine, I$_2$ formation has been found to be more effective in acidic pH values than in neutral or alkaline ones [56]. As I$_2$ acts as a precursor for formation of OM−I compounds [48,49], the possible formation of these compounds and their retention on mineral phase in low pH samples could have an effect on iodine sorption [43]. The transition in the prevailing form from HSeO$_3^-$ to SeO$_3^{2-}$ takes place at approximate pH of 8.4, but pH has no other influence on selenium speciation [132]. For niobium, a marked change in its speciation from neutral Nb(OH)$_5$ to anionic, presumably low−sorbing

$Nb(OH)_6^-$ occurs at the same pH range of 6 - 8 where a sharp decrease in its retention was observed. Furthermore, the retention of niobium was enhanced in MSS in the presence of Ca^{2+} ions compared to calcium free MSS; it is presumed that Ca^{2+} retention on soil surface by outer sphere complexation creates positive surface charge for niobium to adhere to.

4.1.6   EFFECT OF TEMPERATURE (MANUSCRIPT IV, V)

Increase in temperature had no effect on soil retention of iodate or selenate at the temperature range of +8 °C to +38 °C for Olkiluoto mineral soil from the depth of 0.70 m. For these species, the K_d value averaged to 0.57 ± 0.14 ml/g and 0.4 ± 0.3 ml/g, respectively. Iodide retention was not observed at any of the studied temperatures. Slight temperature dependence was detected for the retention of selenite, as the K_d values increased from 46 ± 2 ml/g to 70 ± 4 ml/g and further to 77 ± 12 ml/g at temperature increasing from +8 °C to +22 °C and to +38 °C.

In OM–poor soil environment, iodide and iodate retention has been found to be independent of temperature [56], whereas in OM rich peat environment iodide sorption, as well as selenite sorption, have shown a clear temperature dependence [135,188]. The effect of temperature has proposed to be indirect and act through an increase in the kinetic energy of molecules and in the microbial enzymatic activity responsible for iodide and selenite incorporation into OM [135,188]. The lack of temperature dependence for iodide, iodate and selenate retention can be caused by Olkiluoto mineral soil's low OM content (<1 %), low soil retention of these species or the importance of soil inorganic components in the sorption reactions thus reducing the influence of soil microbes.

4.1.7   EFFECT OF MICROBES (MANUSCRIPT IV, V)

Microbes were observed to have a marked effect on the retention of selenite on Olkiluoto mineral soil as the K_d value decreased from 240 ± 40 ml/g to 89 ± 7 ml/g upon soil sterilisation. The K_d values of selenate, iodide and iodate remained unchanged after sterilisation, indicating that soil microbes or their by–products enzymes did not have a considerable effect on the direct retention of those species in the mineral soil. It is worth mentioning that in this study the reduction of iodate to iodide and formation of presumed OM–I compounds was strongly linked to soil microbial activity (see Chapter 4.2.1 for discussion), even though no microbe–mediated sorption effects were observed. One possibility for the lack of direct sorption effect can be naturally low microbial activity and the rather high initial selenate (7.0×10^{-7} M) and iodine (I^- or IO_3^- at 7.9×10^{-7} M) concentration in the samples, which could have caused the capacity of soil microbial compartment to exceed before discernible sorption changes were observed.

The results for selenate, iodide and iodate are quite opposite to what has been observed previously for soil microbial activity having a notable influence

on the retention of iodine and selenium in soils [36,82,91,101,126,128,134,135,188,196,197]. Typically soil microbial compartment affects selenium by causing speciation changes by the formation of oxidised or preferably reduced forms [82,91,101,135], whereas for iodine the formation of reactive electrophilic I_2 and HIO moieties and their assimilation into OM is microbially catalysed [47,49,53,198].

In Olkiluoto soil microbial activity is most probably concentrated in the OM rich humus layer. Thus, if microbes are to have a meaningful impact on the speciation and/or retention of iodine and selenium in soil, this is to occur places where enrichment of OM is detected, and in soils this indicates the humus layers.

4.1.8   EFFECT OF MINERALOGY (MANUSCRIPTS I, II, IV, V)

Olkiluoto soil minerals exhibited variable retention properties towards cesium, niobium, iodate and selenite. A practical view for comparing the sorption properties of these minerals each having the same grain size of 0.075 – 0.30 mm, was to use SSA corrected K_d values, namely K_a. K_a excludes the effect of variation in the inner and outer SSA of the minerals, and thus weight is on the selectivity of the functional groups and functionalities possessed by the minerals towards the elements under interest.

Of the studied minerals, quartz and potassium feldspar exhibited no sorption of iodate or selenite and only low retention of cesium and niobium. Based on their K_a values (Table 5), the best sorbents in MSS for the studied elements included plagioclase for cesium (2 000 m²/g), hornblende for niobium (150 000 m²/g), chlorite for iodate (16 m²/g) and hematite for selenite (102 m²/g).

Table 5. *SSA corrected K_d values (K_a) for radiotracers [134]Cs and [95]Nb and stable iodate and selenite on the studied Olkiluoto soil minerals (grain size 0.075 – 0.30 mm) as determined in MSS at about pH 8. Iodide sorption was observed only on muscovite (K_a 4.7 m²/g), whereas no retention of selenate was detected on any of the studied minerals.*

MINERAL	K_a (ml/m²)			
	$^{134}Cs^+$	$^{95}Nb(OH)_5^-$	IO_3^-	SeO_3^{2-}
Quartz	21	12 000	0	0
Potassium feldspar	130	1300	0	0
Plagioclase	2000	49 000	0	21.7
Hornblende	174	150 000	0	0
Hematite	150	33 000	9.7	102
Chlorite	57	57 000	16	11.3
Biotite	not determined	2600	12	14.7
Muscovite	1200	53 000	7.1	0

The differences in the retentive properties of the minerals were attributed to their sorption site types (cesium) or surface properties and structural Al and Fe content (iodine, niobium and selenium). For cesium, only low or moderate retention can be expected on minerals having non–specific Si–OH, Al–OH or Fe–OH groups on their surfaces (namely quartz, potassium feldspar, plagioclase, hornblende, hematite), whereas high retention on minerals containing also Cs–specific FES sites is more than likely to occur (muscovite, biotite). Non–specific cation exchange sites are prompt to competition arising from the other cations present in the solution[118,199], and the attraction of ions to these sites increases with increasing charge/radius ratio (increasing charge density) [18,110]. FES sites prefer the retention of cesium over other cations present in the solution due to its low hydration enthalpy leading to capability to shed its hydration water shell upon entering the interlayer space, form inner-sphere complexes with oxygen atoms of siloxane ditrigonal cavities and induce interlayer dehydration and collapse [113]. In MSS, the competition on the muscovite FES sites can presumed to be limited to K^+, but its occupancy of the FES sites was calculated to be very low at 0.3 % (CEC 16.3 µeg/g, FES contribution 0.02 % of CEC, $\log K_c{}^{Cs+}/_{K+} = 5.5$ [118]). In natural soil conditions also the competition on the FES sites arising from the existence of $NH_4{}^+$ ions can hinder the retention of cesium [116].

The situation is rather different for anionic moieties iodate, niobium and selenite, for which retention through inner sphere complexation can occur especially on minerals having considerable fraction of Al–OH and Fe–OH groups on their surfaces involving the replacement of –OH or $–OH_2$ ligands from surface/exposed edge Al or Fe atom by the oxyanion [96,97,105,139-141]. Iodide and selenate are mainly retained by outer sphere complexation (anion exchange), but due to the slightly alkaline pH of about 8, the anion exchange capacity of the minerals can presumed to be non-existent [21]. Furthermore, outer sphere complexation is susceptible to competition of other anions present in the solution [34,60,102,133,138,200]. It is also worth mentioning that for iodine and selenium the presence of structural Fe(II) (e.g. in biotite) can increase retention due to reduction of iodine or selenium to lower oxidation states and formation of chemical bond(s) [33,93,94,96,200]. It is proposed that mineral structure can give indication on the surface (Al+Fe)/Si ratio and thus also on their sorptive properties towards iodate, niobium and selenite by inner sphere complexation reaction: minerals having greater (Al+Fe)/Si ratio (e.g. hornblende, hematite and chlorite) are expected to show higher retention of these elements than those with lower (Al+Fe)/Si ratio (e.g. quartz, potassium feldspar and plagioclase) [109].

From their retentive properties and abundancies in Olkiluoto soil, it is evident that the most important mineral accounting for the retention of cesium in soil is muscovite (K_a 1200 ml/m², abundancy <5 %). Even though weakly crystalline Al and Fe oxides (precursors for crystallized Al and Fe oxides) are not considered as minerals in the absence of continuous three dimensional crystal structure, they bear a significant role for iodine and

selenium soil sorption. Also, muscovite (iodine) and chlorite (selenium) are considered important based on their relatively good sorption properties and abundancy (<5 % for both [22,169,201]) in Olkiluoto soil. Based on the experimental evidence, it is very likely that niobium is retained rather well on all inorganic sorbents present in soil and that similarly to iodine and selenium, weakly crystalline Al and Fe oxides are important sorbents.

4.2 LIQUID PHASE SPECIATION

Iodine and selenium are both redox–sensitive elements prone to alteration in their dominant species as a response to a shift in soil redox potential. Iodine typically exists as a highly mobile iodide in anaerobic, reducing conditions, and its mobility is considered to decrease due to formation of more strongly retained iodate upon soil conditions changing towards more oxidative. Selenium behaves rather differently to iodine, as its mobility increases with increasing redox potential and formation of oxidised selenium form selenate. Iodine and selenium liquid phase speciation was investigated on Olkiluoto mineral soil by varying the experimental conditions e.g. from aerobic to anaerobic and sample material from mineral soil to humus and individual minerals.

4.2.1 IODINE (MANUSCRIPT V)

In the experiments where iodine was initially added as iodide, no formation of iodate was detected in any circumstances similar to the results of previous studies [42,153,189]. This founding indicated iodide to be rather persistent form in the experimental soil conditions, as also suggested by iodine E_h-pH diagram (Figure 1) [44] and preliminary speciation modelling.

Quite oppositely to iodide, iodate was found to be relatively unstable form in the experimental soil conditions as significant reduction into iodide was observed. The fraction of iodate reduced increased with increasing microbial activity, temperature, time and organic matter content, decreasing pH and formation of anaerobic soil conditions. For example, decrease in solution pH from 9 to 4 induced iodide fraction to increase from 0.02 ± 0.01 % to 8.7 ± 0.7 % in aerobic soil conditions and from 12 ± 7 % to 64 ± 9 % in anaerobic soil conditions (Table 6). The reduction of iodate to iodide was assumed to be strongly linked to the presence and action of soil microbes. Indications towards this direction were given by a 3–fold decrease in the iodate reduction percentage upon soil sterilisation; 180–fold increase in the respective percentage upon temperature increase from -22 °C to +8 °C; and 60–fold increase in the reduction percentage when sorbent material changed from aerobic mineral soil to humus. In anaerobic soil conditions, however, the mechanism was thought to be abiotic iodate reduction caused by the decrease in the prevailing redox potential. The average reduced fraction of iodate was

the highest in humus, 37 ± 8 % on average, followed by anaerobic mineral soil (17 ± 19 %) and being the lowest in aerobic mineral soil (0.58 ± 0.7 %). Iodate reduction was observed in the presence of soil mineral phases 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 and muscovite. The ability of soil minerals to induce the formation of iodide was associated to the presence of structural iron (either as Fe(II) or Fe(III)). The unstableness of iodate has been noted previously [33,36,42,49,56,58,153,189,202], and has been observed to be dependent on soil microbial status [36,42] and formation of mildly oxidative or reductive soil conditions [58,153,191,202].

Table 6. *The fraction (%) of iodate reduced into iodide as a function of pH in aerobic and anaerobic soil conditions and the fraction (%) of iodate present from the initial content for aerobic conditions.*

Aerobic soil			Anaerobic soil	
pH	IO_3^- reduction % *	IO_3^- present from the added (%)	**pH**	IO_3^- reduction % [A]
4	8.7±07	53±1	**4**	64±9
5	4.4±0.7	71±1	**5**	59±9
6	1.3±0.1	83±1	**6**	42±11
6.5	0.46±0.1	87±1	**8**	15±8
7	1.6±0.1	88±3	**9**	9.6±15
8	1.3±0.5	89±2	**9.5**	12±7
9	0.02±0.01	90±1		

* calculated from the measured iodide concentration

[A] calculated from the measured iodate concentration due to high unexplained iodide background level

Formation of unidentified, clearly different species from iodide and iodate, was observed for organic matter rich humus samples (peaks 3 and 4 in Figure 16), aerobic mineral soil samples having incubation time of 1 – 21 days and low pH samples of 4 and 5. No unidentified species were detected for anaerobic soil samples in any circumstances. These unidentified species were presumed to present anionic OM−I compounds formed and found rather universally in soils [42,47,48,51,52,57,58,189], except in reducing soil conditions, where OM−I compounds are easily decomposed [43,52,59]. Prerequisite for the formation of OM−I compounds is the presence of sufficient amounts of aromatic carbon and reactive I_2 or HIO species [42,47-52,58], whereas the absence of adequate amounts of aromatic carbon leads to reduction of iodate into iodide [47]. In acidic pH values the activity of biotic and abiotic electron transfer reactions aiming at formation of I_2 (and HIO) and OM−I compounds are at their highest

[53-56]. These factors can partly explain why reduction of iodate to iodide was found simultaneously with the presumed OM–I compounds in aerobic mineral soil samples.
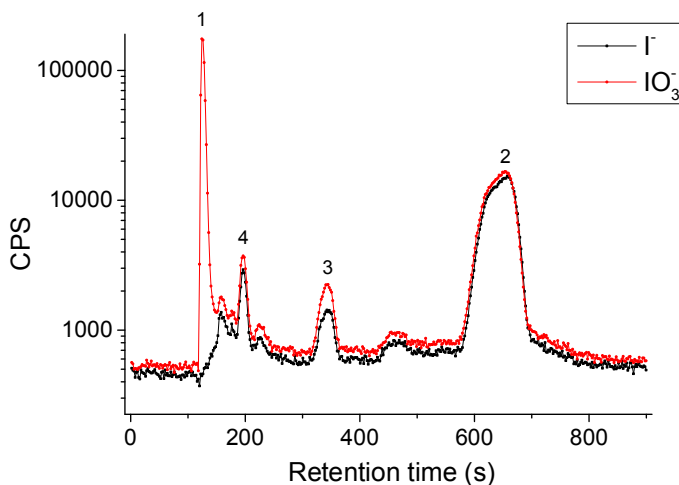

Figure 16. Chromatogram of iodine solutions in the initial chemical form of iodide and iodate contacted with humus for 3–day incubation time. From the chromatograms iodate (1) and iodide (2) peaks can be distinguished. In addition to iodate, iodide and some other small peaks, a clear separation of two unidentified and presumed organo–iodine species (peaks 3 and 4) can be made.

Water–extractable native iodine in iodide form was detected in every background soil sample. However, the native iodide concentration of the aerobic soil samples was below the LOD (1.51 µg/l) of the method. The highest iodide concentrations were leached from humus (average 0.56 ± 0.2 µg/g), followed by anaerobic mineral soil (average 0.065 ± 0.06 µg/g). Interestingly, solution pH had no effect on the water–extractable iodide content of the background mineral soil samples. The higher concentration of native iodide detected in the humus samples is most probably caused by its 50–fold iodine content compared with mineral soil [39], which is not surprising since organic matter has been shown to behave as a principal sorbent for iodine in soils [36-38].

4.2.2   SELENIUM (MANUSCRIPT IV)

Selenite, selenate or any other selenium bearing moieties dissolved or extracted from the background soil samples weas not detected. Both selenite and selenate proved to be persistent forms in the experimental conditions, since selenium liquid–phase speciation was not found to change during the experiments and no unidentified species were detected. Selenium remained in the initial form, either selenite (SeO_3^{2-}) or selenate (SeO_4^{2-}), irrespective of change in incubation time, change in incubation conditions from aerobic to

anaerobic, decrease in microbial activity or variation in temperature. Even though fluctuation in soil reduction potential and the presence of soil microbes has been found to cause reduction/oxidation of selenium in the chain of SeO_4^{2-} ↔ SeO_3^{2-} ↔ $Se(0)$ ↔ $Se(-II)$[82-86,88-91], low presumed microbial activity in Olkiluoto soil samples, presence of more favourable electron acceptors (O_2, NO_3^-) or non–electroactive environment can have led to the absence of noticeable liquid phase speciation changes.

5 CONCLUSIONS

In biosphere safety assessments of the final disposal of spent nuclear fuel, a radioactive plume originated from the repository and migrated through the bedrock is considered entering soil from soil–bedrock interference and proceeding upwards through the soil into soil surface. For such an incidence, soil characteristics and the effects these properties have on radionuclides, can either retard or enhance their migration and soil sorption. In soils, organic matter content and microbial activity, clay fraction content and redox potential, CEC, weakly crystalline Al and Fe oxide content as well as SSA tend to decrease with increasing soil depth, whereas soil pH typically increases. Also, soil forming processes and weathering reactions, such as hydrolysis, dissolution and mineral oxidation–reduction reactions changing soil geological material and forming a base for secondary clay mineral formation are on their most intensive in the surficial parts of regoliths.

In this study soil retention of cesium decreased with soil depth caused by decreasing CEC and SSA. These variables are highly linked to soil clay fraction content – one of soil constituents having a major contribution in cesium retention together with certain clay and mica minerals (e.g. illite, biotite and muscovite) offering Cs–selective FES sites in addition to non–selective ion exchange sites. Cesium retention slightly decreased upon formation of reducing soil conditions, possibly caused by reduction of NO_3^- to NH_4^+ ions and increased competition of the FES sites due to similar size, properties and behaviour of the two cations. Soil organic matter retains cesium very poorly due to low pH at which functional groups remain in their protonated or neutral form, and unspecific retention by outer sphere complexation susceptible to competition from other cations in the solution. Furthermore, the molecules arising from OM can hinder cesium retention on FES sites. Shift in pH towards more alkaline region induces an increase in the retention of cesium on mineral soil caused by an increase in the negative surface charge of soil particles arising from increased deprotonation of surface functional groups. As a combination, these observations would imply cesium to be retained at least to some extent at the most lowest parts of the mineral soil. However, upward movement in a soil profile can be expected until a soil horizon with appropriate redox potential (i.e. no formation of NH_4^+ ions), the highest pH, clay fraction content and FES content as possible and low organic matter content as achievable, is encountered. Time can strengthen the retention of cesium from easily exchangeable form to "fixed", nonreversible form.

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. Humus layer having the highest microbial activity, presented the best retention of inorganic iodine species 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, 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.

Niobium sorption decreased with soil depth together with decreasing CEC, SSA, weakly crystalline Al and Fe oxide content and increasing pH. Colloids generated from the mineral soil were very efficient in retaining niobium, whereas the affinity towards humus–formed colloids was smaller. The importance of aluminium and iron bearing phases in soil retention of niobium together with its low sorption on humus implied the retention to proceed as inner sphere complexation. As a combination these factors would suggest niobium to be retained very efficiently even in highly reducing and slightly alkaline soil conditions possibly met at soil–bedrock interface. If upwards migration in a soil profile occurred, niobium would be retained even more efficiently in aerobic weakly crystalline Al and Fe oxide rich soil layers. Interaction time between niobium and soil components seems to be of a lesser importance.

Selenium soil retention decreased with soil depth as associated with decrease in OM content, CEC, SSA, weakly crystalline Al and Fe oxides, redox potential and increasing pH. Selenite was retained better in the mineral soil than in humus, probably due to the retention mechanism of selenite in soils, inner sphere complexation with Al and Fe surface atoms of their weakly crystalline oxides. Soil microbes have a positive, sorption increasing role in selenite retention, whereas no clear indication of such was observed for

selenate. Inorganic selenium forms, selenate and selenite, seemed to be stable in the experimental conditions, as no selenium liquid phase speciation changes were observed. If for some reason radioactive selenium is to be liberated from the repository and migrated as a plume to bedrock–overburden interface, it is anticipated that the most reduced selenium forms (e.g. Se, Se^{2-}) capable of forming in those hypothetical soil conditions are encountered in the lowest parts of the regolith typically exhibiting the most reducing conditions. If upward migration of selenium, presumably as selenite, is to occur without formation of reduced selenium forms along the flow path, interactions with solid phase materials are to increase with decreasing soil depth and pH and increasing concentration of Al and Fe bearing phases. The interaction strength and sorption is expected to be at its highest in soil layers having the highest abundancy of Al and Fe phases, e.g. their weakly crystalline oxides, and as low pH as possible. Sorption reactions in humus can be of less importance than in mineral soil, but the effect of soil microbes on selenium is considered to be highly important. The formation of OM–Se compounds with variable properties, including the volatile forms enabling the spreading of radioactive selenium further into the biosphere, is likely to occur. Interaction time between selenium and soil components will possibly change selenium speciation in more strongly retained form e.g. from easily exchangeable pool to strongly retained inner sphere complexed reserve.

Importance of soil minerals as sorbents for radioactive cesium, iodine, niobium and selenium depends on the characteristics of the minerals and elements. Cs–selective FES sites present in muscovite (and biotite) interlayer spaces makes it a highly important mineral for cesium retention. Precursor phases for crystalline Al and Fe oxides, soil weakly crystalline Al and Fe oxides, are expected to bear more significance in the retention of inner sphere complexed forms of iodine, niobium and selenium than any specific soil mineral. Furthermore, in boreal forest soil conditions the formation of well–crystalline Al and Fe oxides is not a likely process as organic macromolecules retained on mineral surfaces inhibit the development of ordered crystal structure.

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