Effects of incubation time and filtration method on K_d of indigenous selenium and iodine in temperate soils

T. Almahayni [a], E. H. Bailey [b], N.M.J. Crout [b], G. Shaw [b]
[a] Biosphere Impact Studies, SCK-CEN, Belgian Nuclear Research Centre, Boeretang 200, B-2400 Mol, Belgium
[b] School of Biosciences, University of Nottingham, Sutton Bonington, LE12 5RD, UK

Abstract

In this study, the effects of incubation time and the method of soil solution extraction and filtration on the empirical distribution coefficient (K_d) obtained by de-sorbing indigenous selenium (Se) and iodine (I) from arable and woodland soils under temperate conditions were investigated.

Incubation time had a significant soil- and element-dependent effect on the K_d values, which tended to decrease with the incubation time. Generally, a four-week period was sufficient for the desorption K_d value to stabilise. Concurrent solubilisation of soil organic matter (OM) and release of organically-bound Se and I was probably responsible for the observed decrease in K_d with time. This contrasts with the conventional view of OM as a sink for Se and I in soils. Selenium and I K_d values were not significantly affected by the method of soil solution extraction and filtration.

The results suggest that incubation time is a key criterion when selecting Se and I K_d values from the literature for risk assessments. Values derived from desorption of indigenous soil Se and I might be most appropriate for long-term assessments since they reflect the quasi-equilibrium state of their partitioning in soils.

Key words: Soil indigenous selenium and iodine, distribution coefficient (K_d), incubation time, soil solution extraction, Rhizon soil moisture samplers

1 Introduction

Sorption is a generic term encompassing processes such as adsorption, ion exchange and precipitation. It controls, to a large extent, the transport and accumulation of substances in the environment. The empirical distribution coefficient (K_d) is often used in transport and risk assessment models (e.g. Almahayni, 2014) to aggregate many poorly understood or multi-parameter sorption processes

K_d values are periodically published and updated (e.g. IAEA, 2009; IAEA, 2010). However, published K_d data vary orders of magnitude among soils. This large variation has been partially attributed to the lack of a consistent experimental methodology. Degryse et al. (2009) noted that depending on the methods used to characterise the solid and liquid phases, different K_d values may be obtained. Additionally, the lack of a consistent methodology complicates the comparison of K_d data and may cause confusion when interpreting and applying K_d values in risk assessment models. Factors such as solid-to-liquid ratio, contact time and the extraction and filtration of soil solution are among the main sources of methodological variation between studies determining K_d values.

The solid-to-liquid ratio varies considerably between K_d determination methods. For example, in their review of the sorption coefficients of a suite of elements on iron hydroxides, Li and Kaplan (2012) reported solid-to-liquid ratios that varied over two orders of magnitude. This variation could affect K_d as indicated by Sheppard et al. (2007) who noted that K_d values from batch experiments with a 1:10 soil:water ratio were higher than those from soils incubated at field capacity. As K_d is typically used to estimate retention against leaching, Sheppard et al. (2007) suggested that it is preferable to measure K_d at moisture contents close to, or slightly above, field capacity because that is when leaching occurs. In any case, K_d values should be determined using a solid-to-liquid ratio that is as representative as possible of natural conditions (Limousin et al., 2007).

Contact time between the solid and liquid phases during a K_d experiment often varies between hours and weeks (e.g. Vandenhove and Van Hees, 2007; Sheppard et al., 2009). Short contact times may be ineffectual for measuring the effects of slow (de)sorption mechanisms on K_d. For instance, Ashworth and Shaw (2006a) observed two orders of magnitude increase in $^{125}\mathrm{I}$ K_d during a 7-week mini-column experiment with spiked soils. Recent studies (e.g. Shetaya et al., 2012; Tolu et al., 2014b) have revealed ongoing changes in fractionation and speciation of soil trace elements over periods longer than typical incubation times in short-term K_d experiments.

Of the available methods to extract soil solution, centrifugation is probably the most widely used in K_d experiments (e.g. Xu et al., 2015; Tolu et al., 2014a). ‘Rhizon’ soil moisture samplers have also been used (e.g. Ashworth and Shaw, 2006c; Ashworth et al., 2008). The dissolved phase is operationally defined by the pore size of the membrane used to filter soil solution. Filters of 0.45 µm or 0.22 µm are commonly used to discriminate the dissolved phase from suspended particles.

This study focused on selenium and iodine, both of which have important stable and radio-isotopes. From a non-radiological perspective, deficient or exessive intake of either Se or I can result in serious human or animal health problems (Chen, 2012; Lei et al., 2011; Zimmermann et al., 2008). From a radiological perspective, the radioactive isotopes of Se (^{79}Se, $t_{1/2}$ of 3.27 × 10^5 years) and I (^{129}I, $t_{1/2}$ of 1.61 × 10^7 years) could give rise to additional radiological exposure to humans and non-human biota following their release into the environment (e.g. from waste repositories).

The objectives of this study were to:

a) obtain K_d values for Se and I by de-sorbing indigenous Se and I from soils under realistic moisture conditions;
b) evaluate the effects of incubation time and the method of soil solution extraction and filtration on K_d values of indigenous Se and I.

2 Materials and methods

2.1 Soil sampling and soil characteristics

Soil samples were collected from an arable field and an adjacent mature deciduous woodland strip in the Sutton Bonington area, Leicestershire, UK (52˚49'48"N, 1˚14'23"W). The soils belong to the Wick Soil Series (based on fluvio-glacial sand and gravel overlying Triassic Keuper Marl) with a sandy loam texture. Further details about the study area can be found in Ahmed et al. (2014) and in Shetaya et al. (2012). Soil samples were taken from surface (0-10 cm) and subsurface (40-50 cm) layer of the soil column. All samples were air-dried and sieved (<2 mm) prior to analysis. Selected characteristics of the soils are shown in Table 1.

2.2 Soil incubation experiments

Soil microcosms were prepared as described by Sheppard et al. (2009). Approximately 60 g of air-dried, sieved soil were weighed into a plastic syringe body. Deionised water was slowly added to the syringe to bring the soil to field capacity. The final moisture content at field capacity was approximately 30% for the arable topsoil, subsoil and the woodland subsoil and 45% for the woodland topsoil. All syringes were sealed with a parafilm membrane, to reduce moisture evaporation, and incubated at 10˚C in a temperature-controlled room awaiting sampling.

At the end of the incubation time, the microcosm contents were transferred to a polyoxymethylene (Acetal) centrifuge tube fitted with 20 µm stainless steel mesh filter (Di Bonito et al., 2008) to extract soil solution. These tubes were specially manufactured to fit a Beckman J2-21 refrigerated high speed centrifuge with AJ-10 rotor (r_{max} = 158 mm). The centrifuge buckets were spun at a relative centrifugal field value of 600×*g* for 30 minutes at 4˚C. Centrifugal force pushed the liquid through the stainless steel mesh down to a collection cup. The supernatant was then removed from the collection cups and passed through the appropriate filter.

Selenium and I K_d values determined after 1, 2, 3 and 4 weeks of incubation were compared to investigate the effect of incubation time on K_d. For this experiment, duplicate microcosms (32 in total) were prepared for each combination of soil type and incubation time. Each week, 8 microcosms (2 per soil type) were sampled and their soil solution was extracted by centrifugation then passed through a 0.45 µm filter (Millex® Millipore, Watford, UK) and preserved ready for analyses as described in section 2.3.

Selenium and I K_d values derived from dissolved Se and I concentrations measured in 0.45 µm, 0.22 µm and 0.15 µm soil solution filtrates were compared to investigate the effect of filtration on the K_d of these elements. For this experiment, duplicate microcosms (16 in total) were prepared for each combination of soil type and the 0.22 µm and 0.15 µm filtration levels. The microcosms were incubated for 1 week only, whereupon the soil solution from the 0.22 µm treatment microcosms was extracted by centrifugation and passed through 0.22 µm Millex® Millipore filters and that from the 0.15 µm treatment microcosms was extracted and filtered using Rhizon soil moisture samplers (Eijkelkamp, Netherlands). The K_d data derived from this experiment were combined with K_d data obtained from the 0.45 µm treatment after 1 week of incubation.

Eh was measured in all microcosms immediately prior to soil solution extraction using a calibrated combination electrode (Thermo Scientific ORP glass/platinum electrode) and a high impedance pH/Eh meter. The calibrated electrode was inserted half-way through the wet soil and the reading allowed to stabilise before recording. All values were corrected by adding the standard potential (185 mV) of the combination electrode to the recorded raw potentials.

2.3 Chemical analyses

For the determination of total elemental composition, samples of the sieved soils (< 2 mm) were ground in an agate planetary ball mill before acid digestion. Approximately 250 mg of finely ground soil was digested in PFA Teflon vessels with 2.5 mL hydrofluoric acid (HF; 40% Analytical Reagent), 2 mL nitric acid (HNO_3; 70% Trace Analysis Grade), 1 mL perchloric acid ($HClO_4$; 70% AR) and 2.5 mL H_2O on a 48-place Teflon-coated graphite block digester.

Total soil I was extracted with tetra methyl ammonium hydroxide (TMAH) from finely ground soil samples following the method of Watts and Mitchell (2009).

Soil and soil solution Se, I and multi-elements were determined by ICP-MS (Model X-Series^{II}, Thermo-Fisher Scientific, UK) on the digests after dilution in MQ water. The ICP-MS was operated in collision cell mode (to reduce polyatomic interferences) with hydrogen as the cell gas for Se analyses and 7% hydrogen in helium for the multi-element analyses. For Se analyses, ^{69}Ga, ^{115}In and ^{193}Ir, in 2% HNO_3 and 4% methanol, were used as internal standards (methanol was added to improve the ionisation efficiency, stability and sensitivity of the instrument). For the multi-element analyses, ^{45}Sc, ^{103}Rh and ^{193}Ir in 2% HNO_3 solution were used. Iodine was determined in standard mode using ^{115}In in 1% TMAH solution as internal standard.

Organic carbon in soil solution (DOC) was determined using a Shimadzu total organic carbon analyser (TOC-V_{CPH}) with a non-dispersive infrared detector in non-purgeable organic carbon mode.

The K_d values (L kg^{-1}) were calculated as:

$$K_d = \frac{s}{c}$$

where s (mg kg^{-1}) is the concentration in the dry soil determined from acid and TMAH extractions and c (mg L^{-1}) is the concentration in the extracted soil solution.

Statistical analysis (ANOVA) of the K_d data was carried out on log-transformed data (to remove heteroscedasticity and positive skewness in the data set).

3 Results and discussion

3.1 Total soil Se and I content

Total Se content in the arable and woodland soils (Table 1) was within the range (0.1 to 4 mg kg^{-1}) reported by Broadley et al. (2006) for soils and stream sediments in the UK, but lower than the 0.4 mg kg^{-1} worldwide average (Fordyce, 2013). Total I content was within the 0.5 to 98.2 mg kg^{-1} range reported for British surface soils (Whitehead, 1979) and comparable with the 5 mg kg^{-1} worldwide average for surface soils (Whitehead, 1984).

3.2 Soil redox potential

Soil Eh varied significantly ($p<0.01$) between land use (i.e. arable vs. woodland) and soil type (i.e. topsoil vs. subsoil) as Fig. 1 shows. The mean Eh in the arable topsoil and subsoil was 110 mV and 132 mV lower than in the respective woodland soils. The mean Eh value was also lower in topsoil than in subsoil by about 185 mV in the arable land and 200 mV in the woodland.

Eh decreased significantly ($p<0.01$) with incubation time in the arable topsoil. A maximum decrease of 340 mV was observed between the 1st and 3rd week (Fig. 2). In the woodland topsoil, Eh decreased by 230 mV ($p=0.05$) between 1st and 2nd week; no further decrease in Eh was observed after the 2nd week. Variations in Eh with incubation time in the arable and woodland subsoil were mostly insignificant.

The observed decrease in Eh with incubation time indicates development of anaerobic conditions. The arable and woodland topsoils could be described as moderately reduced soils according to the classification system of Fiedler et al. (2007) and Reddy et al. (2000), which uses the 300 mV Eh value as the boundary between aerobic and anaerobic conditions. The topsoil reduction may have been due to its higher content of readily decomposable OM and associated microflora. Readily decomposable OM has been observed to lower soil Eh, especially in soils with fresh OM (Husson, 2013). In contrast, the subsoil sustained aerobic conditions throughout the incubation.

3.3 Desorption K_d values

The desorption K_d values computed from the concentration of desorbed Se and I in soil solution are summarised in Table 2. The relatively large standard deviation associated with the mean K_d values reflects variation in physicochemical properties of the arable and woodland soils and in the experimental conditions.

The K_d varied significantly between the topsoils and the subsoils. Selenium K_d was higher ($p<0.01$) in the topsoil than in the subsoil by less than a factor of 2 in the arable land and by a factor of 5 in the woodland. Iodine K_d in the topsoil was more than a factor of 3 higher ($p=0.05$) in the arable land and a factor of 4 higher in the woodland (the difference in the woodland was not statistically significant). The higher Se and I K_d values in the topsoils indicate greater retention in these soils compared with the subsoils. This greater retention may be ascribed to the higher OM contents of these soils. Organic matter has a well-recognised role in binding Se and I in soils (Coppin et al., 2006; Coppin et al., 2009; Shetaya et al., 2012; Supriatin et al., 2015).

The K_d values of indigenous Se in Table 2 tend to be ~~are consistently~~ higher than those reported in the literature from sorption of exogenous (i.e. freshly added) Se in soils with a similar texture. For instance, the mean K_d value in Table 2 for the arable topsoil is higher than the in–situ 5 L kg^{-1} and 46 L kg^{-1} values determined by Ashworth and Shaw (2006b) from sorption of ^{75}Se in a sandy loam topsoil under different soil water regimes. The value in Table 2 is also higher than the 138 L kg^{-1} and 116 L kg^{-1} values determined by Ashworth et al. (2008) from sorption of ^{75}Se in clay loam and sandy loam topsoils. The mean K_d value of indigenous Se in the woodland topsoil is slightly lower than the 274 L kg^{-1} value determined by Ashworth et al. (2008) from sorption of ^{75}Se in a woodland topsoil. Furthermore, the mean K_d values for the arable and woodland topsoils in Table 2 are higher, within the experimental error, than the mean K_d value (200 L kg^{-1}, n=172) reported in the IAEA (2010) compendium for a wide range of soils and experimental conditions.

For indigenous I, the mean K_d value in Table 2 for the arable topsoil is higher than the 2 L kg^{-1} and 7 L kg^{-1} values determined by Ashworth and Shaw (2006a) from sorption of ^{125}I in a sandy loam topsoil. Iodine K_d values presented in Table 2 are also considerably higher than these reported by Shetaya et al. (2012) for sorption of ^{129}I in the arable and woodland soils, which were obtained by fitting a range of mathematical models (e.g. (ir)reversible first order and spherical diffusion models) to experimental data. Additionally, the mean K_d values for all soils in Table 2 are higher than the mean K_d value (7 L kg^{-1}, n=250) reported in the IAEA (2010) compendium for a wide range of soils and experimental conditions.

The higher K_d values of indigenous Se and I could be partially ascribed to slow fixation (i.e. aging) of these elements in the arable and woodland soils. Aging has been shown to control Se and I mobility in soils. Li et al. (2016) observed that while the available Se (soluble + exchangeable) fraction decreased over time in their Se-spiked soils, the fractions of organically-bound and residual Se increased. They attributed the decrease in the available fraction to multiple processes (e.g. diffusion, precipitation, occlusion by organic matter) as a diffusion-based model did not fit their experimental data satisfactorily. Shetaya et al. (2012) demonstrated that inorganic I inputs into the arable and woodland soils were assimilated into solid phase humus at varying rates depending on the speciation of the input (e.g. iodide or iodate) and soil OC content. Similar behaviour was observed for soil metals. For instance, Lu et al. (2005) contaminated three Chinese soils of varying characteristics with lead (Pb), zinc (Zn), copper (Cu) and cadmium (Cd) and monitored the change in their fractionation over a period of 8 weeks. Their experiment revealed a time-dependent decrease in the exchangeable fraction, which was simulated successfully using a diffusion model, in contrast to a consistent increase in the fractions bound to soil Fe and OM. Jalali and Khanlari (2008) reported a decrease with time in the exchangeable fraction of exogenous Pb, Zn, Cd and Cu added to calcareous soils.

3.4 Effect of incubation time on desorption K_d

Variations in K_d with incubation time in the arable and woodland soils are shown in Figs. 3 and 4. Generally, the K_d decreased significantly (p<0.05) with incubation time in the topsoil. For Se, the maximum decrease, by a factor of 5, was observed in the woodland topsoil between the 1st and 3rd week. In the arable topsoil, the variations were small and insignificant. For I, the maximum decrease, by a factor of 34, was observed in the woodland topsoil between 1st and 3rd week. A smaller decrease in I K_d (by a factor of 17) was observed in the arable topsoil over the same period. Variations in Se and I K_d with incubation time in the subsoil were small and insignificant.

Overall, a 4-week incubation time was sufficient for Se and I desorption to reach a quasi-steady state in the arable and woodland soils. This time frame is comparable with the reference equilibration time proposed by Li et al. (2016) for Se ageing in three Chinese soils. A four-week period was also sufficient to attain equilibrium for the sorption of $^{125}\mathrm{I}$ in sandy loam soils (Ashworth and Shaw, 2006a) and for the sorption of $^{125}\mathrm{I}^{-}$ and $^{125}\mathrm{IO}_3^{-}$ species in Savannah River Site sediments (Xu et al., 2015).

The decrease in K_d with time in the topsoil was probably driven by gradual release into soil solution of Se and I bound to OM. This hypothesis is supported by the observed time-dependent increase in DOC concentration in the arable and woodland soils (Fig. 5), and by the positive and significant (Pearson) correlation between the K_d values of Se and I and those of OC in the arable topsoil (r=0.66; p=0.02 for Se and r=0.80; p<0.01 for I) and in the woodland topsoil (r=0.97; p<0.01 for Se and r=0.90; p<0.01 for I). These results imply that soil OM could act not only as a sink for Se and I but also as a source for these elements in soil solution. This role of soil OM and the mechanisms involved have already been demonstrated and described by many researchers (Grybos et al., 2007; Grybos et al., 2009; Li et al., 2014; Xu et al., 2011b).

The decrease in K_d with time coincided with an increase in dissolved Fe concentrations in soil solution (Fig. 6). The K_d values of Se and I positively and significantly correlated with the K_d values of Fe in the arable topsoil (r=0.61; p=0.04 for Se and r=0.63; p=0.03 for I) and in the woodland topsoil (r=0.96; p<0.01 for Se and r=0.95; p<0.01 for I). Interestingly, no significant correlations were found between the K_d values of these elements in mineral subsoil, which possibly suggests that the correlation with the K_d values of Fe in the topsoil might have been indirectly caused by the OM. In fact, the K_d values of Fe and OC in the topsoil were positively correlated ($r \geq 0.68$; p<0.05).

3.5 Effect of extraction and filtration method on K_d

Selenium and I K_d values from the different solution extraction and filtration methods are shown in Figs. 7A and 7B. Neither the extraction method (i.e. centrifugation vs. Rhizon moisture samplers) nor the filter pore sizes appear to have had a significant effect on Se and I K_d values.

Previous studies have shown that colloidal Se and I may represent a considerable fraction of total Se and I concentrations in soil solution. For instance, up to 86% of Se in extracts from a wide range of Dutch grassland topsoils was most likely bound to or incorporated in 1 nm to 0.45 µm colloidal-sized OM (Weng et al., 2010). Xu et al. (2011a) demonstrated the formation of colloidal I (3 kDa to 0.45 µm) in Savannah River Site soils amended with ^{125}I in the form of iodide and iodate. The lack of a significant filtration effect on Se and I K_d values in our soils, however, possibly indicates that the fraction of colloidal Se and I was small or that colloidal Se and I were mainly smaller than 0.15 µm in size.

4 Conclusions

K_d values of indigenous Se and I were determined for temperate arable and woodland soils under field capacity conditions. The values varied significantly between soils, and were typically higher for soils with higher OM. The K_d values determined in this study from desorption of indigenous Se and I were consistently higher than those reported in the literature from short-term sorption experiments.

The effects of two methodological factors on the K_d values of Se and I were evaluated, namely a) the incubation time and b) the soil solution extraction and filtration method. The effects of these methodological factors were soil and element dependent. In the topsoil, the K_d decreased significantly with the incubation time; the decrease in K_d was greater for I than for Se. Overall, a four-week incubation time was sufficient for the K_d value to stabilise. In the subsoil, the variations in K_d with time were small and insignificant. Selenium and I K_d values did not vary significantly with the pore size of the filter used to discriminate between the solid and liquid phases, indicating that dissolved Se and I were probably associated with small colloids (<0.15 µm).

Our results confirm the important role of OM in controlling Se and I mobility in soils. In contrast to the conventional view of OM as a major sink for trace elements in soils, our results suggest that OM could, under certain conditions, release Se and I into soil solution.

Finally, our results suggest that the variation in Se and I K_d with soil depth calls for careful consideration of soil properties (mainly OM in the case of Se and I) when selecting K_d values for modelling their transport and accumulation in soils. Higher K_d values might be required to reflect Se and I accumulation in topsoil enriched in OM in comparison with mineral subsoils. Another consideration for modelling purposes is the simulation time frame. Arguably, desorption K_d values might be more appropriate than short-term sorption K_d values for simulating the long-term mobility of Se and I in soils because they reflect the quasi-steady state distribution of these elements in soils.

5 References

Ahmed, H., Young, S. D. & Shaw, G. 2014. Factors affecting uranium and thorium fractionation and profile distribution in contrasting arable and woodland soils. *Journal of Geochemical Exploration,* 145**,** 98-105.

Almahayni, T. 2014. A comparison between the Example Reference Biosphere model ERB 2B and a process-based model: simulation of a natural release scenario. *Journal of Environmental Radioactivity,* 138**,** 279-288.

Ashworth, D., Moore, J. & Shaw, G. 2008. Effects of soil type, moisture content, redox potential and methyl bromide fumigation on K d values of radio-selenium in soil. *Journal of environmental radioactivity,* 99**,** 1136-1142.

Ashworth, D. & Shaw, G. 2006a. Effects of moisture content and redox potential on in situ K d values for radioiodine in soil. *Science of the total environment,* 359**,** 244-254.

Ashworth, D. & Shaw, G. 2006b. Soil migration, plant uptake and volatilisation of radio-selenium from a contaminated water table. *Science of the total environment,* 370**,** 506-514.

Ashworth, D. J. & Shaw, G. 2006c. Effects of moisture content and redox potential on in situ Kd values for radioiodine in soil. *Science of The Total Environment,* 359**,** 244-254.

Broadley, M. R., White, P. J., Bryson, R. J., Meacham, M. C., Bowen, H. C., Johnson, S. E., Hawkesford, M. J., McGrath, S. P., Zhao, F.-J., Breward, N., Harriman, M. & Tucker, M. 2006. Biofortification of UK food crops with selenium. *The Proceedings of the Nutrition Society,* 65**,** 169-181.

Chen, J. 2012. An original discovery: Selenium deficiency and Keshan disease (an endemic heart disease).

Coppin, F., Chabroullet, C. & Martin-Garin, A. 2009. Selenite interactions with some particulate organic and mineral fractions isolated from a natural grassland soil. *European Journal of Soil Science,* 60**,** 369-376.

Coppin, F., Chabroullet, C., Martin-Garin, A., Balesdent, J. & Gaudet, J.-P. 2006. Methodological approach to assess the effect of soil ageing on selenium behaviour: first results concerning mobility and solid fractionation of selenium. *Biology and Fertility of Soils,* 42**,** 379-386.

Degryse, F., Smolders, E. & Parker, D. 2009. Partitioning of metals (Cd, Co, Cu, Ni, Pb, Zn) in soils: concepts, methodologies, prediction and applications–a review. *European Journal of Soil Science,* 60**,** 590-612.

Di Bonito, M., Breward, N., Crout, N., Smith, B. & Young, S. 2008. Overview of selected soil pore water extraction methods for the determination of potentially toxic elements in contaminated soils: operational and technical aspects. *Environmental Geochemistry: Site Characterization, Data Analysis, Case Histories. Elsevier***,** 213-249.

Fiedler, S., Vepraskas, M. J. & Richardson, J. 2007. Soil redox potential: importance, field measurements, and observations. *Advances in Agronomy,* 94**,** 1-54.

Fordyce, F. M. 2013. Selenium deficiency and toxicity in the environment. *Essentials of medical geology.* Netherlands: Springer

Grybos, M., Davranche, M., Gruau, G. & Petitjean, P. 2007. Is trace metal release in wetland soils controlled by organic matter mobility or Fe-oxyhydroxides reduction? *Journal of Colloid and Interface Science,* 314**,** 490-501.

Grybos, M., Davranche, M., Gruau, G., Petitjean, P. & Pédrot, M. 2009. Increasing pH drives organic matter solubilization from wetland soils under reducing conditions. *Geoderma,* 154**,** 13-19.

Husson, O. 2013. Redox potential (Eh) and pH as drivers of soil/plant/microorganism systems: a transdisciplinary overview pointing to integrative opportunities for agronomy. *Plant and Soil,* 362**,** 389-417.

IAEA 2009. Quantification of radionuclide transfer in terrestrial and freshwater environments for radiological assessments. TECDOC No. 1616 Vienna: International Atomic Energy Agency.

IAEA 2010. Handbook of parameter values for the prediction of radionuclides transfer in terrestrial and freshwaters environments. *Technical Report Series No. 472.* Vienna: International Atomic Energy Agency.

Jalali, M. & Khanlari, Z. 2008. Effect of aging process on the fractionation of heavy metals in some calcareous soils of Iran. *Geoderma,* 143**,** 26-40.

Lei, C., Niu, X., Ma, X. & Wei, J. 2011. Is selenium deficiency really the cause of Keshan disease? *Environmental Geochemistry and Health,* 33**,** 183-188.

Li, D. & Kaplan, D. I. 2012. Sorption coefficients and molecular mechanisms of Pu, U, Np, Am and Tc to Fe (hydr)oxides: A review. *Journal of Hazardous Materials,* 243**,** 1-18.

Li, J., Peng, Q., Liang, D., Liang, S., Chen, J., Sun, H., Li, S. & Lei, P. 2016. Effects of aging on the fraction distribution and bioavailability of selenium in three different soils. *Chemosphere,* 144**,** 2351-2359.

Li, J., Wang, Y., Guo, W., Xie, X., Zhang, L., Liu, Y. & Kong, S. 2014. Iodine mobilization in groundwater system at Datong basin, China: evidence from hydrochemistry and fluorescence characteristics. *Science of the Total Environment,* 468**,** 738-745.

Limousin, G., Gaudet, J.-P., Charlet, L., Szenknect, S., Barthes, V. & Krimissa, M. 2007. Sorption isotherms: a review on physical bases, modeling and measurement. *Applied Geochemistry,* 22**,** 249-275.

Lu, A., Zhang, S. & Shan, X.-q. 2005. Time effect on the fractionation of heavy metals in soils. *Geoderma,* 125**,** 225-234.

Reddy, K. R., D'Angelo, E. M. & Harris, W. G. 2000. Biogeochemistry of wetlands. *In:* SUMNER, M. E. (ed.) *Handbook of Soil Science.* Boca Raton, FL: CRC Press.

Sheppard, M. I., Sheppard, S. C. & Grant, C. a. 2007. Solid/liquid partition coefficients to model trace element critical loads for agricultural soils in Canada. *Canadian Journal of Soil Science,* 87**,** 189-201.

Sheppard, S., Long, J., Sanipelli, B. & Sohlenius, G. 2009. *Solid/liquid partition coefficients (Kd) for selected soils and sediments at Forsmark and Laxemar-Simpevarp*, Svensk kärnbränslehantering (SKB).

Shetaya, W. H., Young, S. D., Watts, M. J., Ander, E. L. & Bailey, E. H. 2012. Iodine dynamics in soils. *Geochimica et Cosmochimica Acta,* 77**,** 457-473.

Supriatin, S., Weng, L. & Comans, R. N. J. 2015. Selenium speciation and extractability in Dutch agricultural soils. *Science of The Total Environment,* 532**,** 368-382.

Tolu, J., Di Tullo, P., Le Hécho, I., Thiry, Y., Pannier, F., Potin-Gautier, M. & Bueno, M. 2014a. A new methodology involving stable isotope tracer to compare simultaneously short-and long-term selenium mobility in soils. *Analytical and bioanalytical chemistry,* 406**,** 1221-1231.

Tolu, J., Thiry, Y., Bueno, M., Jolivet, C., Potin-Gautier, M. & Le Hécho, I. 2014b. Distribution and speciation of ambient selenium in contrasted soils, from mineral to organic rich. *Science of The Total Environment,* 479**,** 93-101.

Vandenhove, H. & Van Hees, M. 2007. Predicting radium availability and uptake from soil properties. *Chemosphere,* 69**,** 664-674.

Watts, M. J. & Mitchell, C. J. 2009. A pilot study on iodine in soils of Greater Kabul and Nangarhar provinces of Afghanistan *Environmental Geochemistry and Health,* 31**,** 503–509.

Weng, L., Vega, F. A., Supriatin, S., Bussink, W. & Riemsdijk, W. H. V. 2010. Speciation of Se and DOC in soil solution and their relation to Se bioavailability. *Environmental science & technology,* 45**,** 262-267.

Whitehead, D. C. 1979. Iodine in the U.K. environment with particular reference to agriculture. *Journal of Applied Ecology,* 16**,** 269-279.

Whitehead, D. C. 1984. The distribution and transformations of iodine in the environment. *Environment International,* 10**,** 321-339.

Xu, C., Kaplan, D. I., Zhang, S., Athon, M., Ho, Y.-F., Li, H.-P., Yeager, C. M., Schwehr, K. A., Grandbois, R. & Wellman, D. 2015. Radioiodine sorption/desorption and speciation transformation by subsurface sediments from the Hanford Site. *Journal of environmental radioactivity,* 139**,** 43-55.

Xu, C., Miller, E. J., Zhang, S., Li, H.-P., Ho, Y.-F., Schwehr, K. A., Kaplan, D. I., Otosaka, S., Roberts, K. A. & Brinkmeyer, R. 2011a. Sequestration and remobilization of radioiodine (129I) by soil organic matter and possible consequences of the remedial action at Savannah River Site. *Environmental science & technology,* 45**,** 9975-9983.

Xu, C., Zhang, S., Ho, Y.-F., Miller, E. J., Roberts, K. A., Li, H.-P., Schwehr, K. A., Otosaka, S., Kaplan, D. I. & Brinkmeyer, R. 2011b. Is soil natural organic matter a sink or source for mobile radioiodine (129 I) at the

Savannah River Site? *Geochimica et Cosmochimica Acta,* 75**,** 5716-5735.

Zimmermann, M. B., Jooste, P. L. & Pandav, C. S. 2008. Iodine-deficiency disorders. *The Lancet,* 372**,** 1251-1262.

6 Tables

Table 1 Major characteristics of the arable and woodland soils. Iron and Se were determined in acid extracts, whereas I was determined in TMAH extracts.

	pH	**OC**	**Fe**	**Se**	**I**
		%	mg kg^{-1}	mg kg^{-1}	mg kg^{-1}
Arable topsoil	7.3	2.24	10382	0.27	4.87
Arable subsoil	6.8	0.79	8517	0.20	2.35
Wood topsoil	4.3	10.1	7475	0.33	4.41
Wood subsoil	3.8	1.66	7121	0.10	1.98

Table 2 Summary statistics of desorption K_d (L kg^{-1}) values for Se and I data determined across all incubation times and filter pore sizes. Standard deviation of the mean (n=12) is given in parenthesis.

	Land use	**Soil**	**Median**	**Mean**	**Min**	**Max**
Se	Arable	Topsoil	177	176 (49)	103	252
		Subsoil	122	123 (32)	59	169
	Woodland	Topsoil	148	268 (232)	90	789
		Subsoil	51	52 (6)	41	61
I	Arable	Topsoil	83	84 (64)	5	176
		Subsoil	24	23 (7)	9	32
	Woodland	Topsoil	21	73 (105)	4	281
		Subsoil	17	16 (2)	13	18

7 Figures

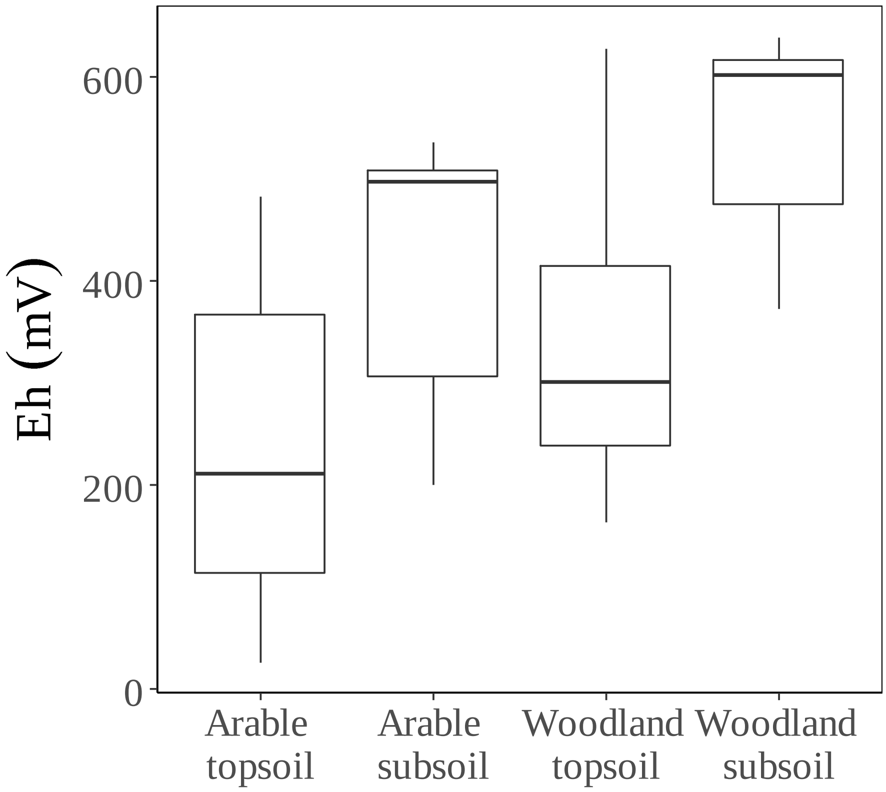

Fig. 1 Variation in Eh between soils. Data represent values measured during the 4-week incubation. The thick horizontal line is the median, edges of the box are the upper and lower quartiles, the vertical lines are the whiskers.

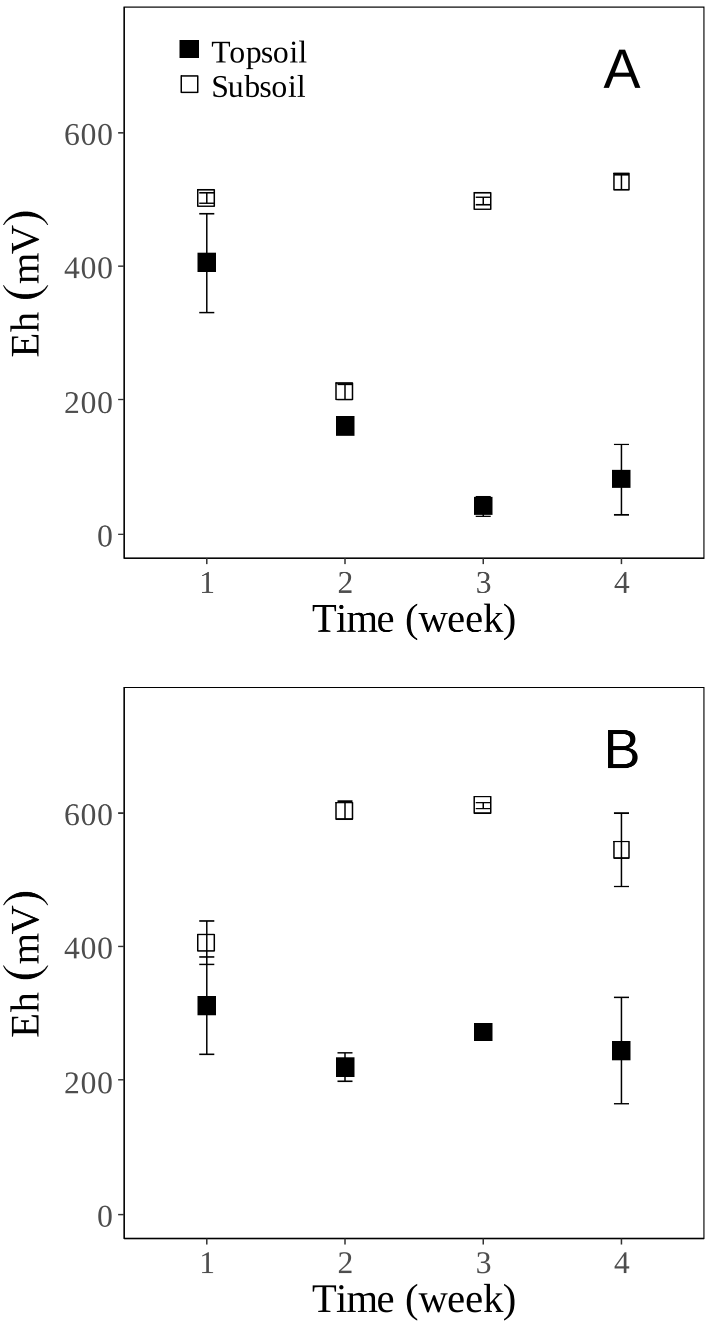

Fig. 2 Variation in mean Eh (±standard error) with incubation time in (A) arable and (B) woodland soils. For the 1st week, values from all filtrates were combined (n=6).

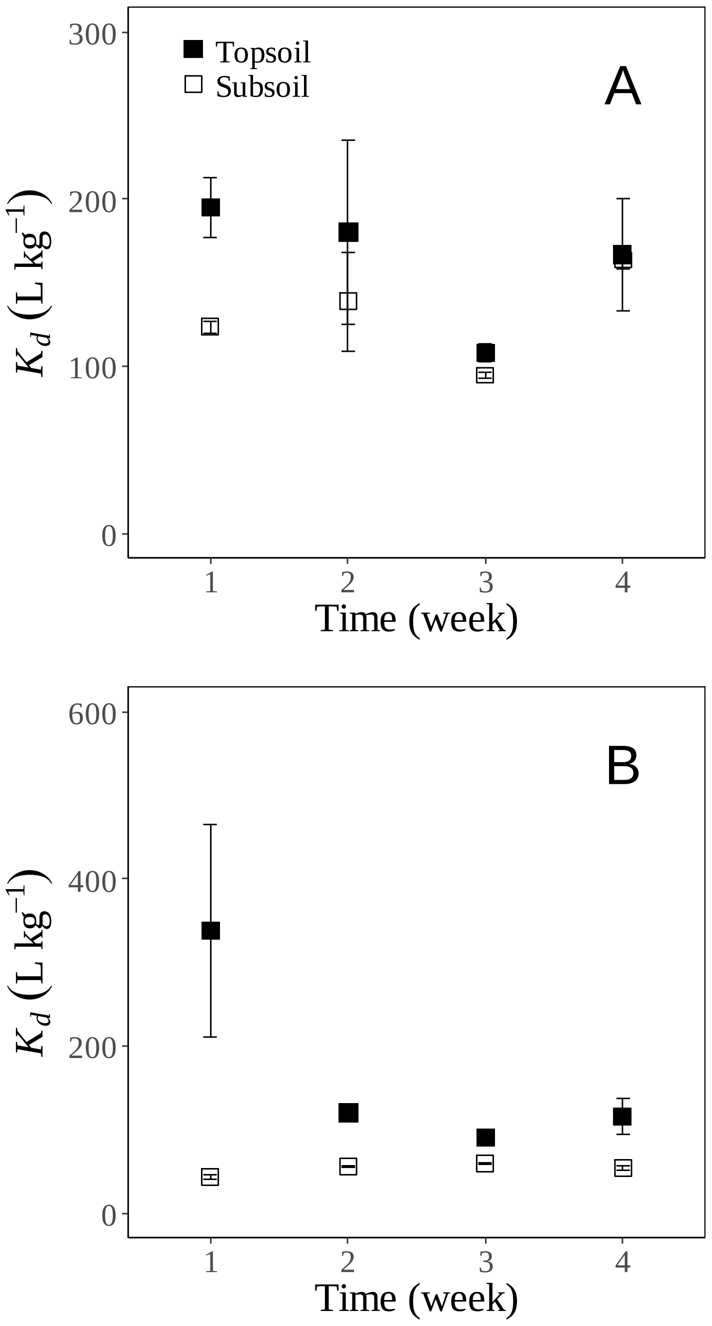

Fig. 3 Variation in mean (± standard error) Se desorption K_d with incubation time in (A) arable and (B) woodland soils.

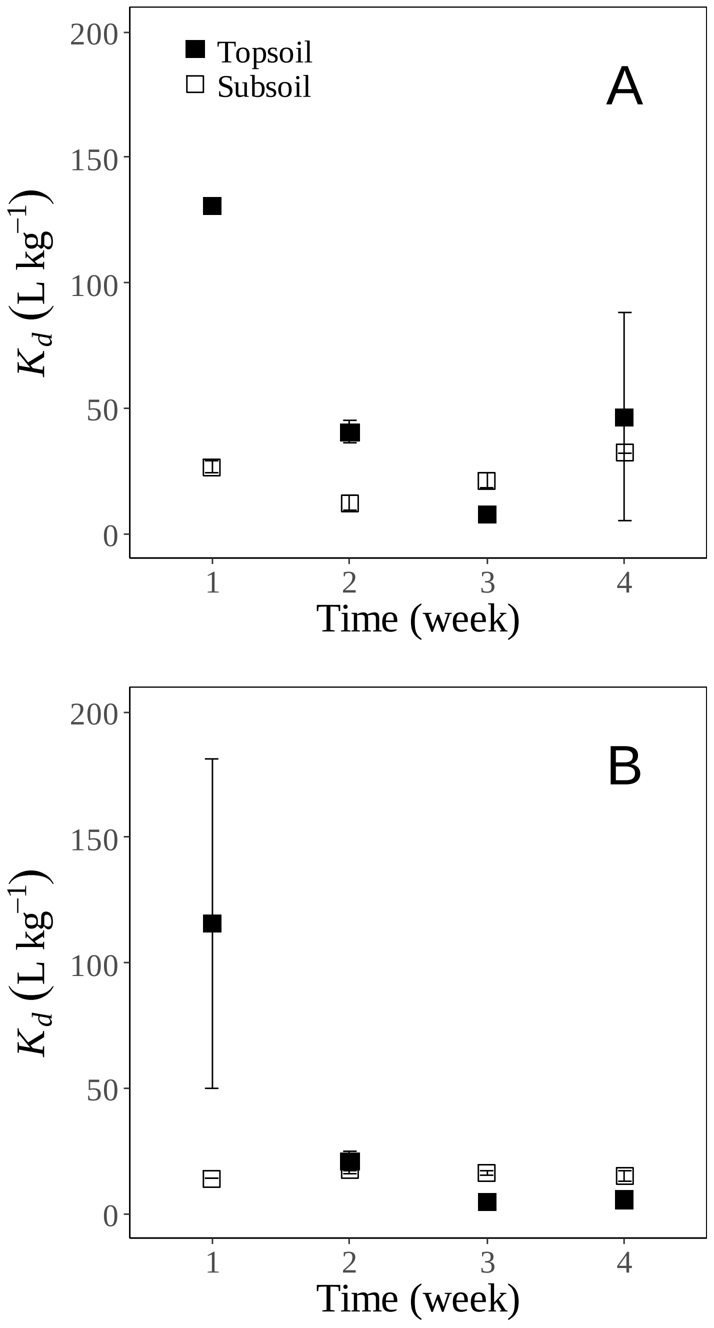

Fig. 4 Variation in mean (± standard error) I desorption K_d with incubation time in (A) arable and (B) woodland soils.

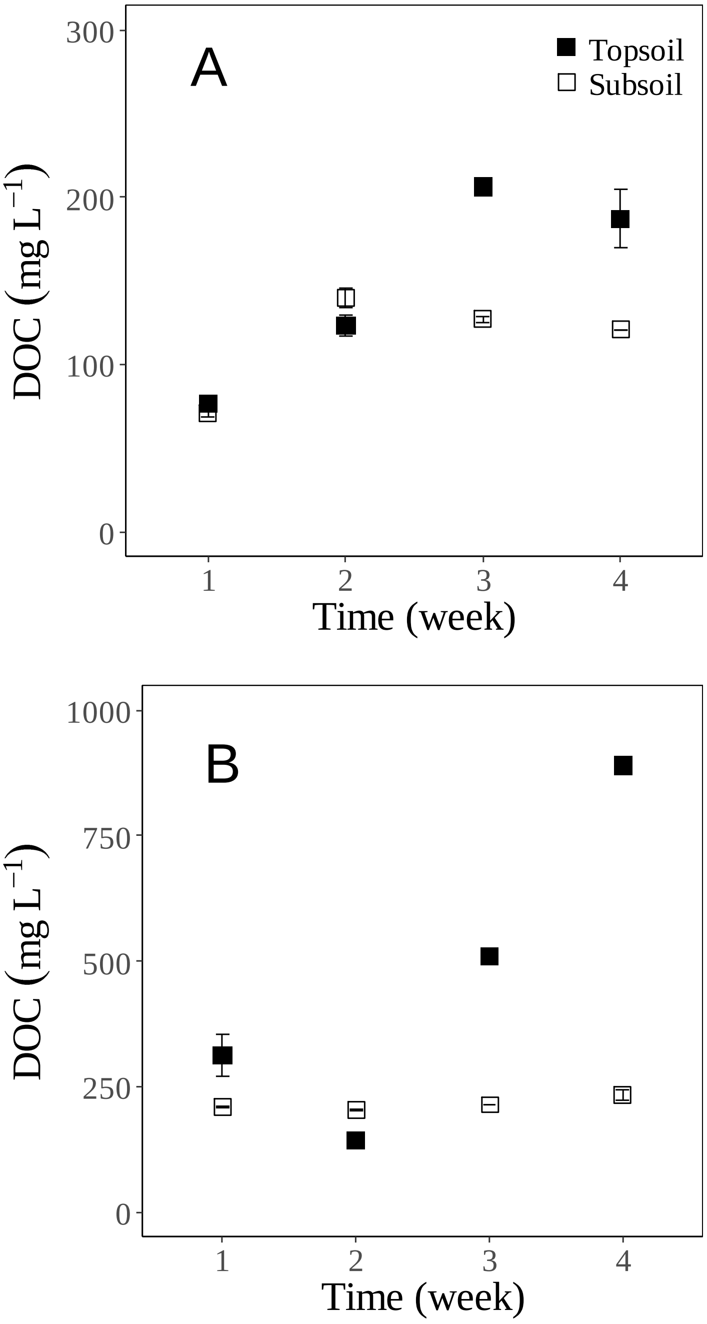

Fig. 5 Variation in mean (± standard error) DOC concentration with incubation time in (A) arable and (B) woodland soils.

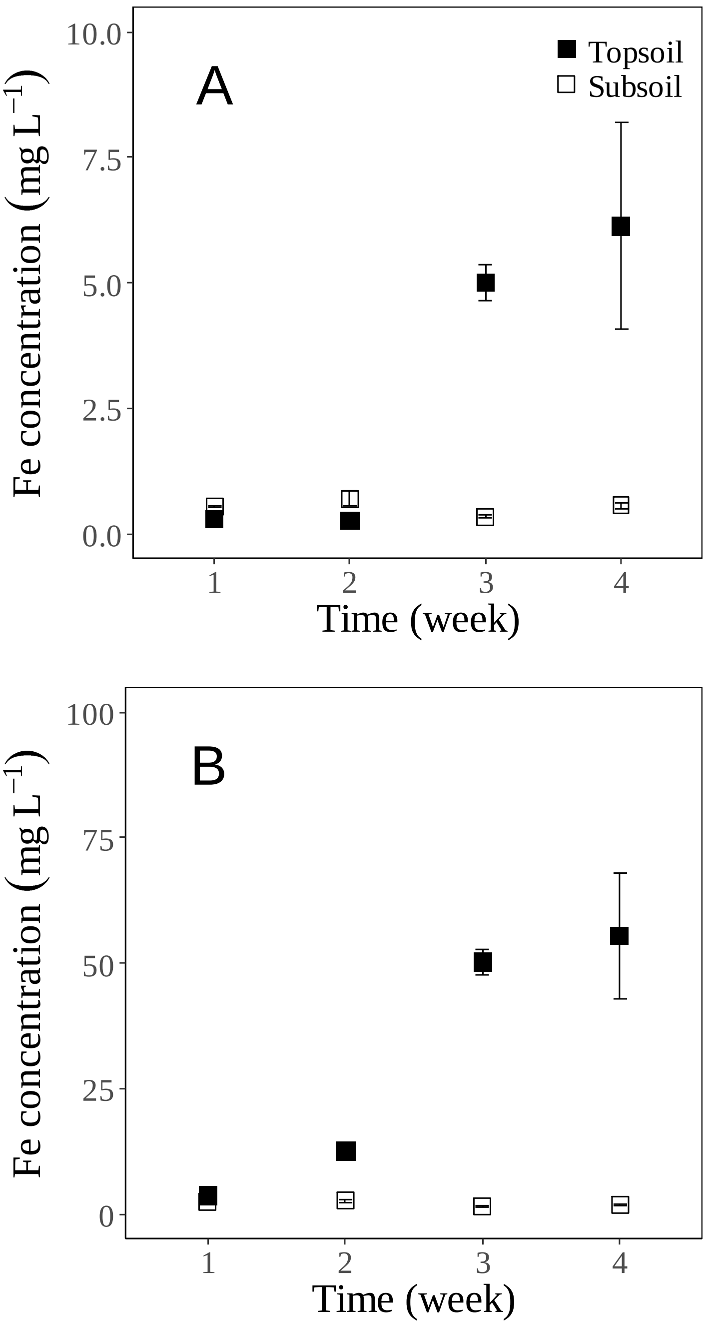

Fig. 6 Variation in mean (± standard error) Fe concentration in soil solution with incubation time in (A) arable and (B) woodland soils.

485

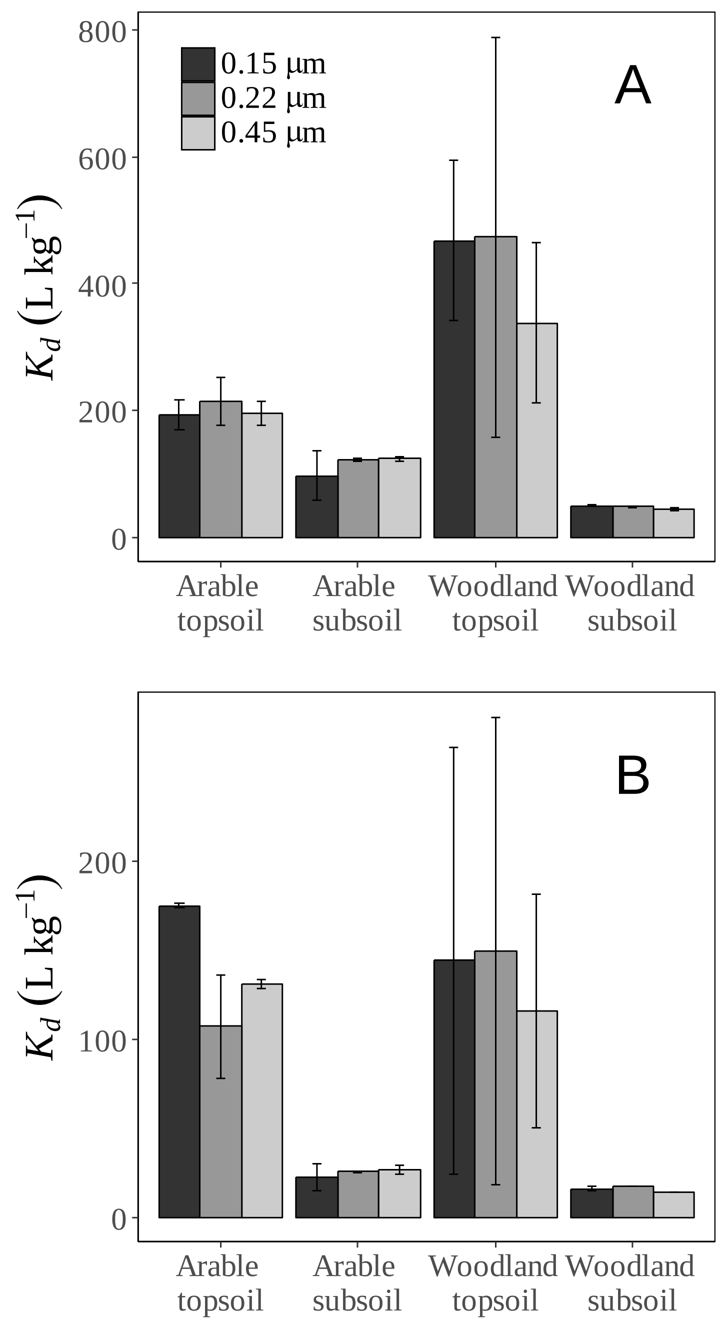

Fig. 7 Variation in mean (± standard error) desorption K_d values between 0.45 µm 0.22 µm and 0.15 µm filtrates for (A) Se and (B) I.