

# 1 Effects of incubation time and filtration method on $K_d$ of 2 indigenous selenium and iodine in temperate soils

3 T. Almahayni <sup>a</sup>, E. H. Bailey <sup>b</sup>, N.M.J. Crout <sup>b</sup>, G. Shaw <sup>b</sup>

4 <sup>a</sup> Biosphere Impact Studies, SCK-CEN, Belgian Nuclear Research Centre,  
5 Boeretang 200, B-2400 Mol, Belgium

6 <sup>b</sup> School of Biosciences, University of Nottingham, Sutton Bonington, LE12  
7 5RD, UK

## 8 Abstract

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

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

21 The results suggest that incubation time is a key criterion when selecting Se  
22 and I  $K_d$  values from the literature for risk assessments. Values derived from  
23 desorption of indigenous soil Se and I might be most appropriate for long-term

24 assessments since they reflect the quasi-equilibrium state of their partitioning  
25 in soils.

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

## 28 **1 Introduction**

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

35  $K_d$  values are periodically published and updated (e.g. IAEA, 2009; IAEA,  
36 2010). However, published  $K_d$  data vary orders of magnitude among soils. This  
37 large variation has been partially attributed to the lack of a consistent  
38 experimental methodology. Degryse et al. (2009) noted that depending on the  
39 methods used to characterise the solid and liquid phases, different  $K_d$  values  
40 may be obtained. Additionally, the lack of a consistent methodology  
41 complicates the comparison of  $K_d$  data and may cause confusion when  
42 interpreting and applying  $K_d$  values in risk assessment models. Factors such as  
43 solid-to-liquid ratio, contact time and the extraction and filtration of soil solution  
44 are among the main sources of methodological variation between studies  
45 determining  $K_d$  values.

46 The solid-to-liquid ratio varies considerably between  $K_d$  determination methods.  
47 For example, in their review of the sorption coefficients of a suite of elements  
48 on iron hydroxides, Li and Kaplan (2012) reported solid-to-liquid ratios that  
49 varied over two orders of magnitude. This variation could affect  $K_d$  as indicated  
50 by Sheppard et al. (2007) who noted that  $K_d$  values from batch experiments  
51 with a 1:10 soil:water ratio were higher than those from soils incubated at field

52 capacity. As  $K_d$  is typically used to estimate retention against leaching,  
53 Sheppard et al. (2007) suggested that it is preferable to measure  $K_d$  at moisture  
54 contents close to, or slightly above, field capacity because that is when leaching  
55 occurs. In any case,  $K_d$  values should be determined using a solid-to-liquid ratio  
56 that is as representative as possible of natural conditions (Limousin et al.,  
57 2007).

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

67 Of the available methods to extract soil solution, centrifugation is probably the  
68 most widely used in  $K_d$  experiments (e.g. Xu et al., 2015; Tolu et al., 2014a).  
69 'Rhizon' soil moisture samplers have also been used (e.g. Ashworth and Shaw,  
70 2006c; Ashworth et al., 2008). The dissolved phase is operationally defined by  
71 the pore size of the membrane used to filter soil solution. Filters of 0.45  $\mu\text{m}$  or  
72 0.22  $\mu\text{m}$  are commonly used to discriminate the dissolved phase from  
73 suspended particles.

74 This study focused on selenium and iodine, both of which have important stable  
75 and radio-isotopes. From a non-radiological perspective, deficient or excessive

76 intake of either Se or I can result in serious human or animal health problems  
77 (Chen, 2012; Lei et al., 2011; Zimmermann et al., 2008). From a radiological  
78 perspective, the radioactive isotopes of Se ( $^{79}\text{Se}$ ,  $t_{1/2}$  of  $3.27 \times 10^5$  years) and I  
79 ( $^{129}\text{I}$ ,  $t_{1/2}$  of  $1.61 \times 10^7$  years) could give rise to additional radiological exposure  
80 to humans and non-human biota following their release into the environment  
81 (e.g. from waste repositories).

82 The objectives of this study were to:

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

## 87 **2 Materials and methods**

### 88 **2.1 Soil sampling and soil characteristics**

89 Soil samples were collected from an arable field and an adjacent mature  
90 deciduous woodland strip in the Sutton Bonington area, Leicestershire, UK  
91 ( $52^\circ 49' 48''\text{N}$ ,  $1^\circ 14' 23''\text{W}$ ). The soils belong to the Wick Soil Series (based on  
92 fluvio-glacial sand and gravel overlying Triassic Keuper Marl) with a sandy loam  
93 texture. Further details about the study area can be found in Ahmed et al.  
94 (2014) and in Shetaya et al. (2012). Soil samples were taken from surface (0-  
95 10 cm) and subsurface (40-50 cm) layer of the soil column. All samples were  
96 air-dried and sieved (<2 mm) prior to analysis. Selected characteristics of the  
97 soils are shown in Table 1.

## 98 2.2 Soil incubation experiments

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

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

116 Selenium and I  $K_d$  values determined after 1, 2, 3 and 4 weeks of incubation  
117 were compared to investigate the effect of incubation time on  $K_d$ . For this  
118 experiment, duplicate microcosms (32 in total) were prepared for each  
119 combination of soil type and incubation time. Each week, 8 microcosms (2 per  
120 soil type) were sampled and their soil solution was extracted by centrifugation

121 then passed through a 0.45  $\mu\text{m}$  filter (Millex® Millipore, Watford, UK) and  
122 preserved ready for analyses as described in section 2.3.

123 Selenium and I  $K_d$  values derived from dissolved Se and I concentrations  
124 measured in 0.45  $\mu\text{m}$ , 0.22  $\mu\text{m}$  and 0.15  $\mu\text{m}$  soil solution filtrates were  
125 compared to investigate the effect of filtration on the  $K_d$  of these elements. For  
126 this experiment, duplicate microcosms (16 in total) were prepared for each  
127 combination of soil type and the 0.22  $\mu\text{m}$  and 0.15  $\mu\text{m}$  filtration levels. The  
128 microcosms were incubated for 1 week only, whereupon the soil solution from  
129 the 0.22  $\mu\text{m}$  treatment microcosms was extracted by centrifugation and passed  
130 through 0.22  $\mu\text{m}$  Millex® Millipore filters and that from the 0.15  $\mu\text{m}$  treatment  
131 microcosms was extracted and filtered using Rhizon soil moisture samplers  
132 (Eijkelkamp, Netherlands). The  $K_d$  data derived from this experiment were  
133 combined with  $K_d$  data obtained from the 0.45  $\mu\text{m}$  treatment after 1 week of  
134 incubation.

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

### 141 **2.3 Chemical analyses**

142 For the determination of total elemental composition, samples of the sieved  
143 soils (< 2 mm) were ground in an agate planetary ball mill before acid digestion.  
144 Approximately 250 mg of finely ground soil was digested in PFA Teflon vessels

145 with 2.5 mL hydrofluoric acid (HF; 40% Analytical Reagent), 2 mL nitric acid  
146 (HNO<sub>3</sub>; 70% Trace Analysis Grade), 1 mL perchloric acid (HClO<sub>4</sub>; 70% AR) and  
147 2.5 mL H<sub>2</sub>O on a 48-place Teflon-coated graphite block digester.

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

150 Soil and soil solution Se, I and multi-elements were determined by ICP-MS  
151 (Model X-Series<sup>II</sup>, Thermo-Fisher Scientific, UK) on the digests after dilution in  
152 MQ water. The ICP-MS was operated in collision cell mode (to reduce  
153 polyatomic interferences) with hydrogen as the cell gas for Se analyses and 7%  
154 hydrogen in helium for the multi-element analyses. For Se analyses, <sup>69</sup>Ga, <sup>115</sup>In  
155 and <sup>193</sup>Ir, in 2% HNO<sub>3</sub> and 4% methanol, were used as internal standards  
156 (methanol was added to improve the ionisation efficiency, stability and  
157 sensitivity of the instrument). For the multi-element analyses, <sup>45</sup>Sc, <sup>103</sup>Rh and  
158 <sup>193</sup>Ir in 2% HNO<sub>3</sub> solution were used. Iodine was determined in standard mode  
159 using <sup>115</sup>In in 1% TMAH solution as internal standard.

160 Organic carbon in soil solution (DOC) was determined using a Shimadzu total  
161 organic carbon analyser (TOC-V<sub>CPH</sub>) with a non-dispersive infrared detector in  
162 non-purgeable organic carbon mode.

163 The  $K_d$  values (L kg<sup>-1</sup>) were calculated as:

164 
$$K_d = \frac{s}{c}$$

165 where  $s$  (mg kg<sup>-1</sup>) is the concentration in the dry soil determined from acid and  
166 TMAH extractions and  $c$  (mg L<sup>-1</sup>) is the concentration in the extracted soil



167 solution.

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

## 170 **3 Results and discussion**

### 171 **3.1 Total soil Se and I content**

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

### 178 **3.2 Soil redox potential**

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

184 Eh decreased significantly ( $p < 0.01$ ) with incubation time in the arable topsoil. A  
185 maximum decrease of 340 mV was observed between the 1<sup>st</sup> and 3<sup>rd</sup> week (Fig.  
186 2). In the woodland topsoil, Eh decreased by 230 mV ( $p = 0.05$ ) between 1<sup>st</sup> and  
187 2<sup>nd</sup> week; no further decrease in Eh was observed after the 2<sup>nd</sup> week. Variations

188 in Eh with incubation time in the arable and woodland subsoil were mostly  
189 insignificant.

190 The observed decrease in Eh with incubation time indicates development of  
191 anaerobic conditions. The arable and woodland topsoils could be described as  
192 moderately reduced soils according to the classification system of Fiedler et al.  
193 (2007) and Reddy et al. (2000), which uses the 300 mV Eh value as the  
194 boundary between aerobic and anaerobic conditions. The topsoil reduction may  
195 have been due to its higher content of readily decomposable OM and  
196 associated microflora. Readily decomposable OM has been observed to lower  
197 soil Eh, especially in soils with fresh OM (Husson, 2013). In contrast, the subsoil  
198 sustained aerobic conditions throughout the incubation.

### 199 **3.3 Desorption $K_d$ values**

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

205 The  $K_d$  varied significantly between the topsoils and the subsoils. Selenium  $K_d$   
206 was higher ( $p<0.01$ ) in the topsoil than in the subsoil by less than a factor of 2  
207 in the arable land and by a factor of 5 in the woodland. Iodine  $K_d$  in the topsoil  
208 was more than a factor of 3 higher ( $p=0.05$ ) in the arable land and a factor of 4  
209 higher in the woodland (the difference in the woodland was not statistically  
210 significant). The higher Se and I  $K_d$  values in the topsoils indicate greater  
211 retention in these soils compared with the subsoils. This greater retention may

212 be ascribed to the higher OM contents of these soils. Organic matter has a well-  
213 recognised role in binding Se and I in soils (Coppin et al., 2006; Coppin et al.,  
214 2009; Shetaya et al., 2012; Supriatin et al., 2015).

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

229 For indigenous I, the mean  $K_d$  value in Table 2 for the arable topsoil is higher  
230 than the 2 L kg<sup>-1</sup> and 7 L kg<sup>-1</sup> values determined by Ashworth and Shaw (2006a)  
231 from sorption of <sup>125</sup>I in a sandy loam topsoil. Iodine  $K_d$  values presented in Table  
232 2 are also considerably higher than these reported by Shetaya et al. (2012) for  
233 sorption of <sup>129</sup>I in the arable and woodland soils, which were obtained by fitting  
234 a range of mathematical models (e.g. (ir)reversible first order and spherical  
235 diffusion models) to experimental data. Additionally, the mean  $K_d$  values for all

236 soils in Table 2 are higher than the mean  $K_d$  value ( $7 \text{ L kg}^{-1}$ ,  $n=250$ ) reported in  
237 the IAEA (2010) compendium for a wide range of soils and experimental  
238 conditions.

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

### 259 3.4 Effect of incubation time on desorption $K_d$

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

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

276 The decrease in  $K_d$  with time in the topsoil was probably driven by gradual  
277 release into soil solution of Se and I bound to OM. This hypothesis is supported  
278 by the observed time-dependent increase in DOC concentration in the arable  
279 and woodland soils (Fig. 5), and by the positive and significant (Pearson)  
280 correlation between the  $K_d$  values of Se and I and those of OC in the arable  
281 topsoil ( $r=0.66$ ;  $p=0.02$  for Se and  $r=0.80$ ;  $p<0.01$  for I) and in the woodland  
282 topsoil ( $r=0.97$ ;  $p<0.01$  for Se and  $r=0.90$ ;  $p<0.01$  for I). These results imply that

283 soil OM could act not only as a sink for Se and I but also as a source for these  
284 elements in soil solution. This role of soil OM and the mechanisms involved  
285 have already been demonstrated and described by many researchers (Grybos  
286 et al., 2007; Grybos et al., 2009; Li et al., 2014; Xu et al., 2011b).

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

### 296 **3.5 Effect of extraction and filtration method on $K_d$**

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

301 Previous studies have shown that colloidal Se and I may represent a  
302 considerable fraction of total Se and I concentrations in soil solution. For  
303 instance, up to 86% of Se in extracts from a wide range of Dutch grassland  
304 topsoils was most likely bound to or incorporated in 1 nm to 0.45  $\mu\text{m}$  colloidal-  
305 sized OM (Weng et al., 2010). Xu et al. (2011a) demonstrated the formation of  
306 colloidal I (3 kDa to 0.45  $\mu\text{m}$ ) in Savannah River Site soils amended with  $^{125}\text{I}$  in

307 the form of iodide and iodate. The lack of a significant filtration effect on Se and  
308 I  $K_d$  values in our soils, however, possibly indicates that the fraction of colloidal  
309 Se and I was small or that colloidal Se and I were mainly smaller than 0.15  $\mu\text{m}$   
310 in size.

## 311 **4 Conclusions**

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

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

328 Our results confirm the important role of OM in controlling Se and I mobility in  
329 soils. In contrast to the conventional view of OM as a major sink for trace

330 elements in soils, our results suggest that OM could, under certain conditions,  
331 release Se and I into soil solution.

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



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- 474

475 **6 Tables**

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

	<b>pH</b>	<b>OC</b> %	<b>Fe</b> mg kg <sup>-1</sup>	<b>Se</b> mg kg <sup>-1</sup>	<b>I</b> mg kg <sup>-1</sup>
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

478

Table 2 Summary statistics of desorption  $K_d$  (L kg<sup>-1</sup>) 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.

	<b>Land use</b>	<b>Soil</b>	<b>Median</b>	<b>Mean</b>	<b>Min</b>	<b>Max</b>
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

479

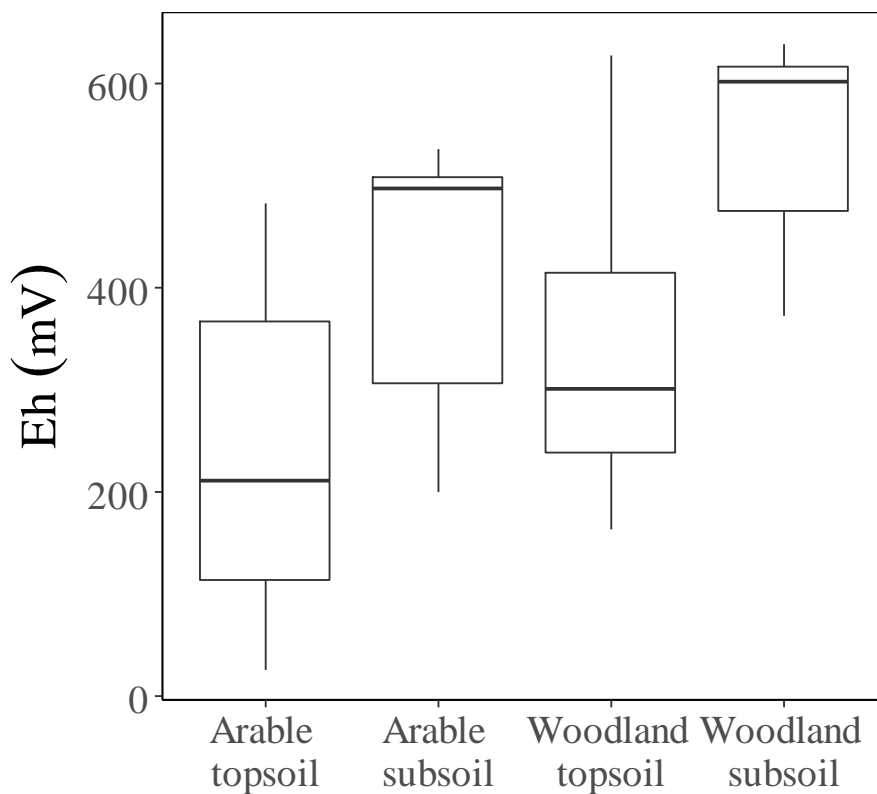


Fig. 1 Variation in Eh between soils. Data represent values measured during the 4-week incubation. The thick horizontal line is the median, edges of the box are the upper and lower quartiles, the vertical lines are the whiskers.

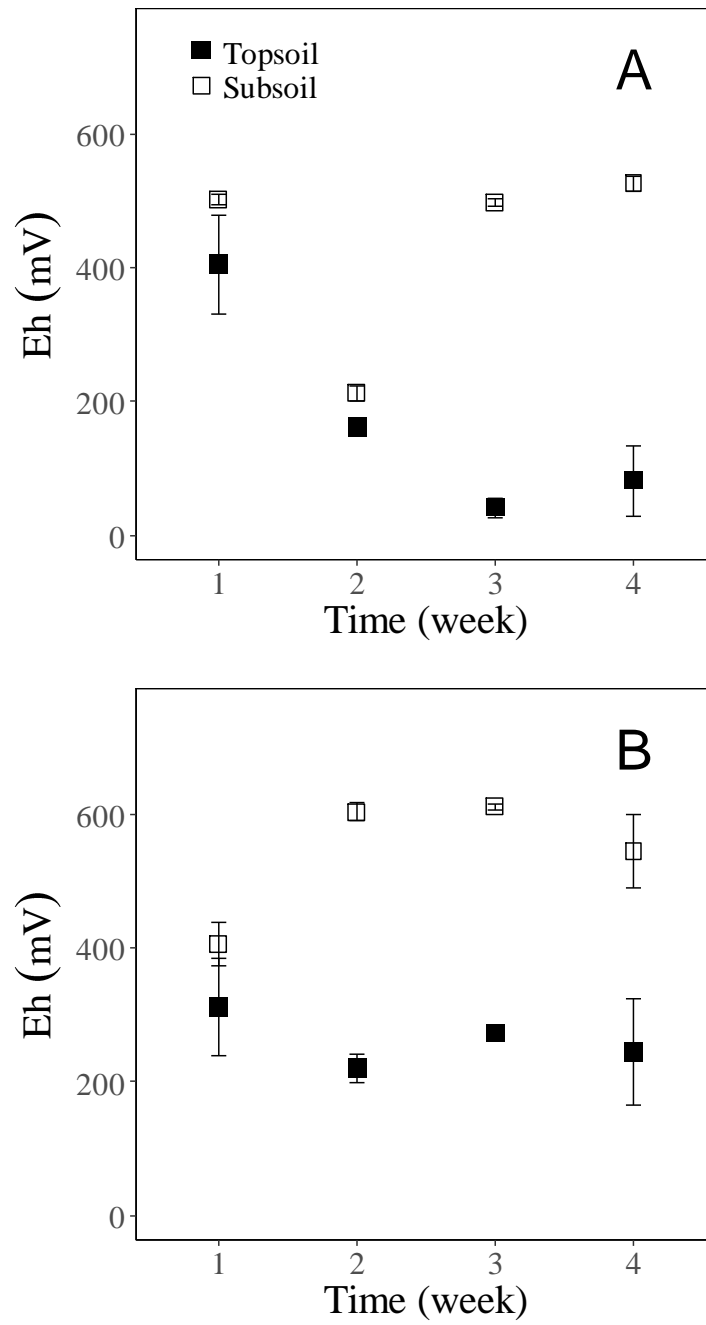


Fig. 2 Variation in mean Eh ( $\pm$ standard error) with incubation time in (A) arable and (B) woodland soils. For the 1<sup>st</sup> week, values from all filtrates were combined (n=6).



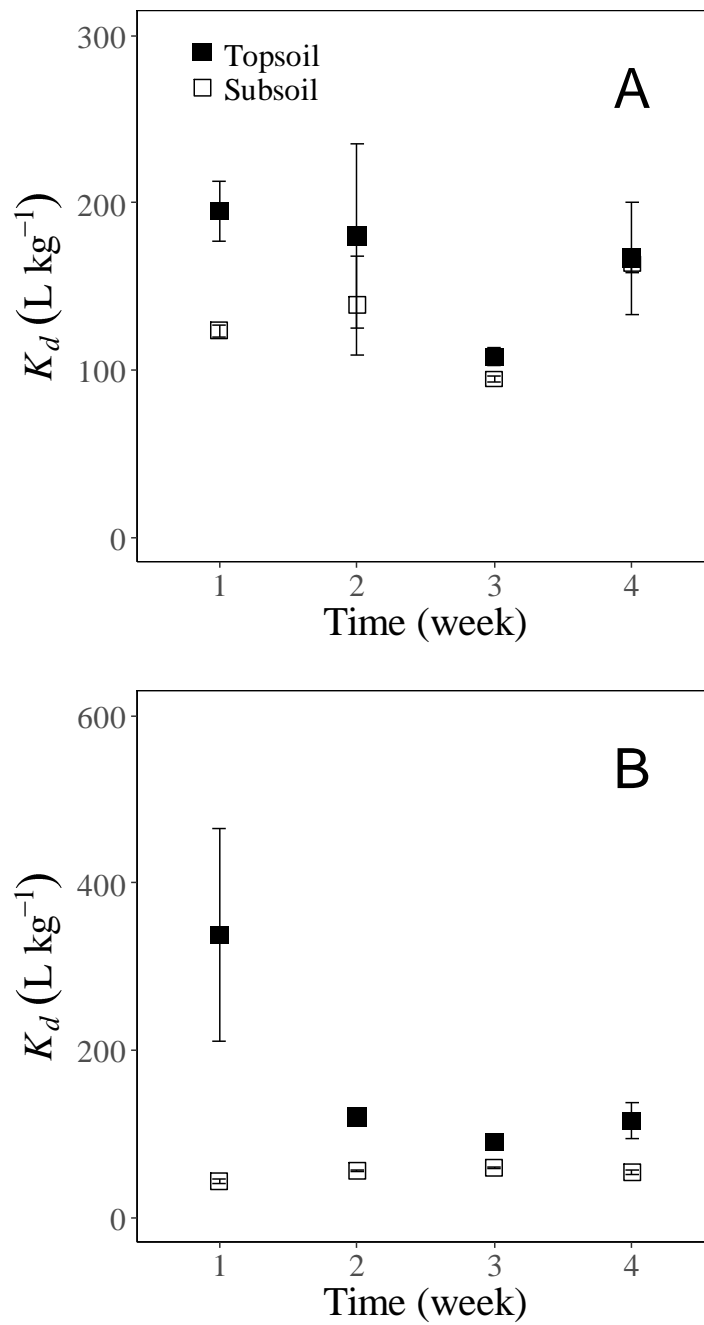


Fig. 3 Variation in mean ( $\pm$  standard error) Se desorption  $K_d$  with incubation time in (A) arable and (B) woodland soils.

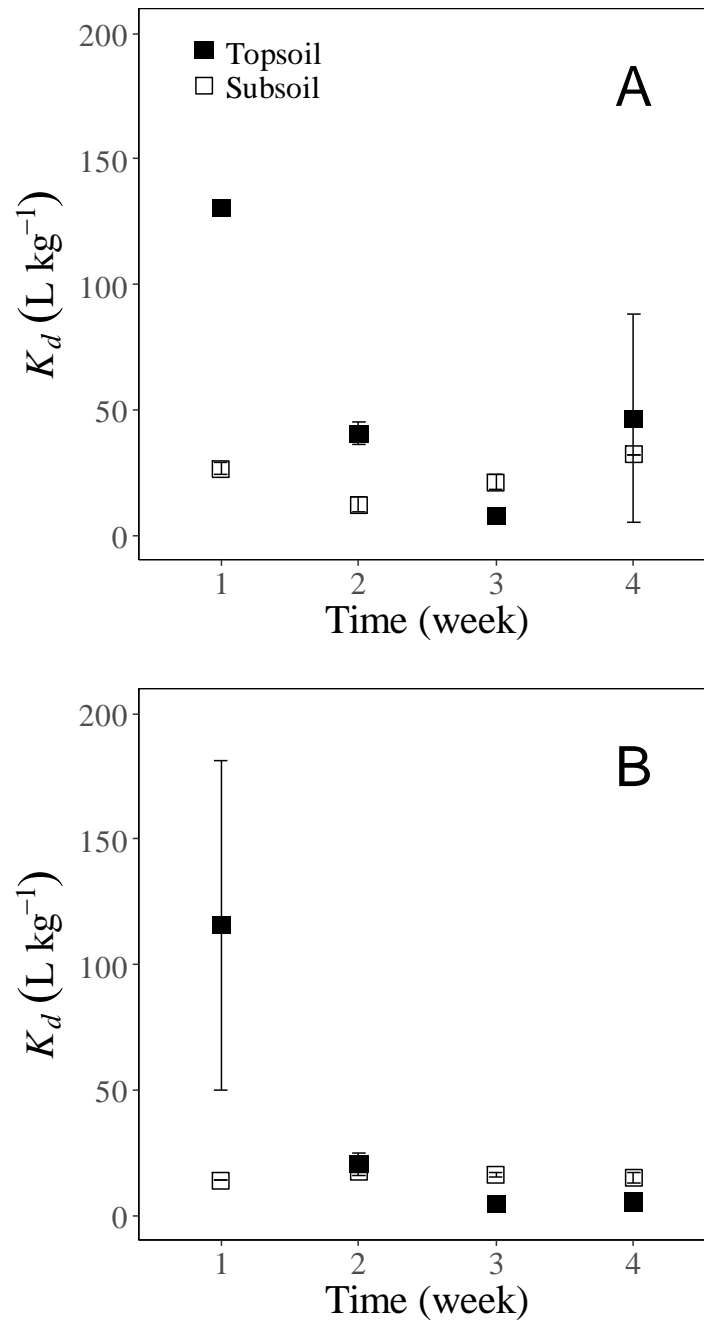


Fig. 4 Variation in mean ( $\pm$  standard error) I desorption  $K_d$  with incubation time in (A) arable and (B) woodland soils.

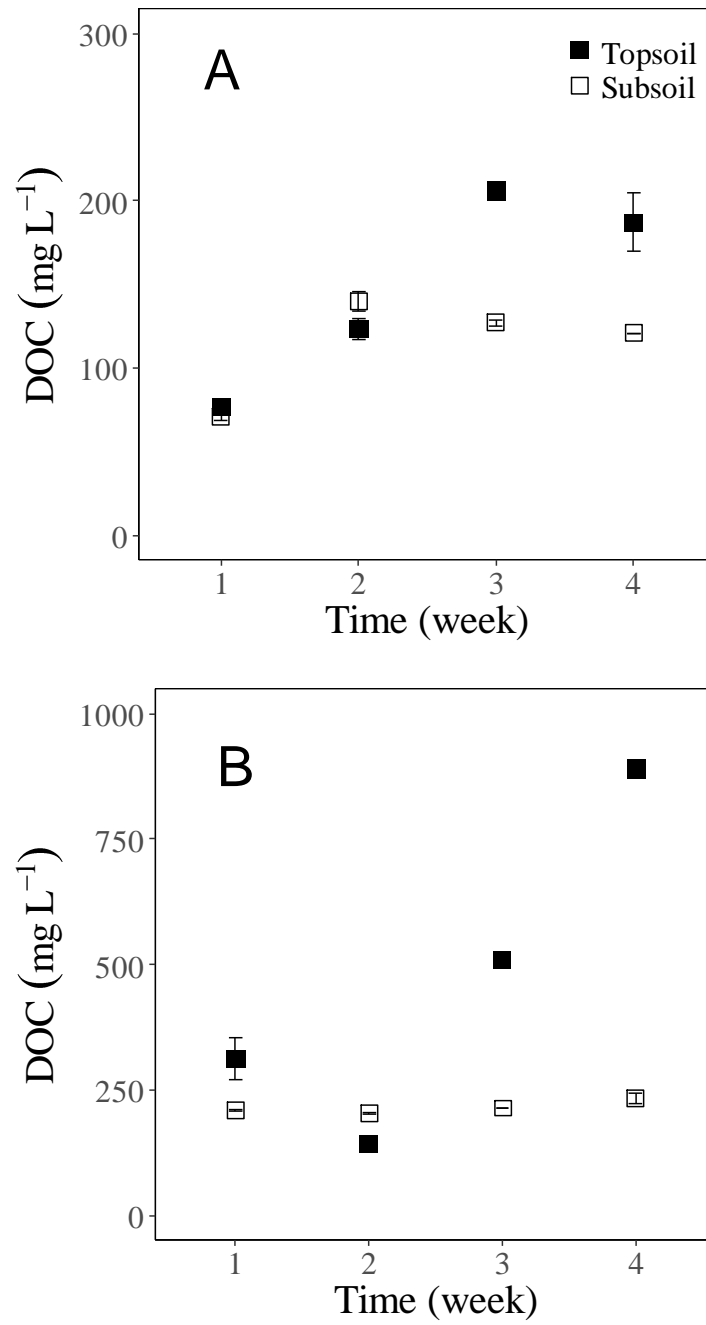


Fig. 5 Variation in mean ( $\pm$  standard error) DOC concentration with incubation time in (A) arable and (B) woodland soils.

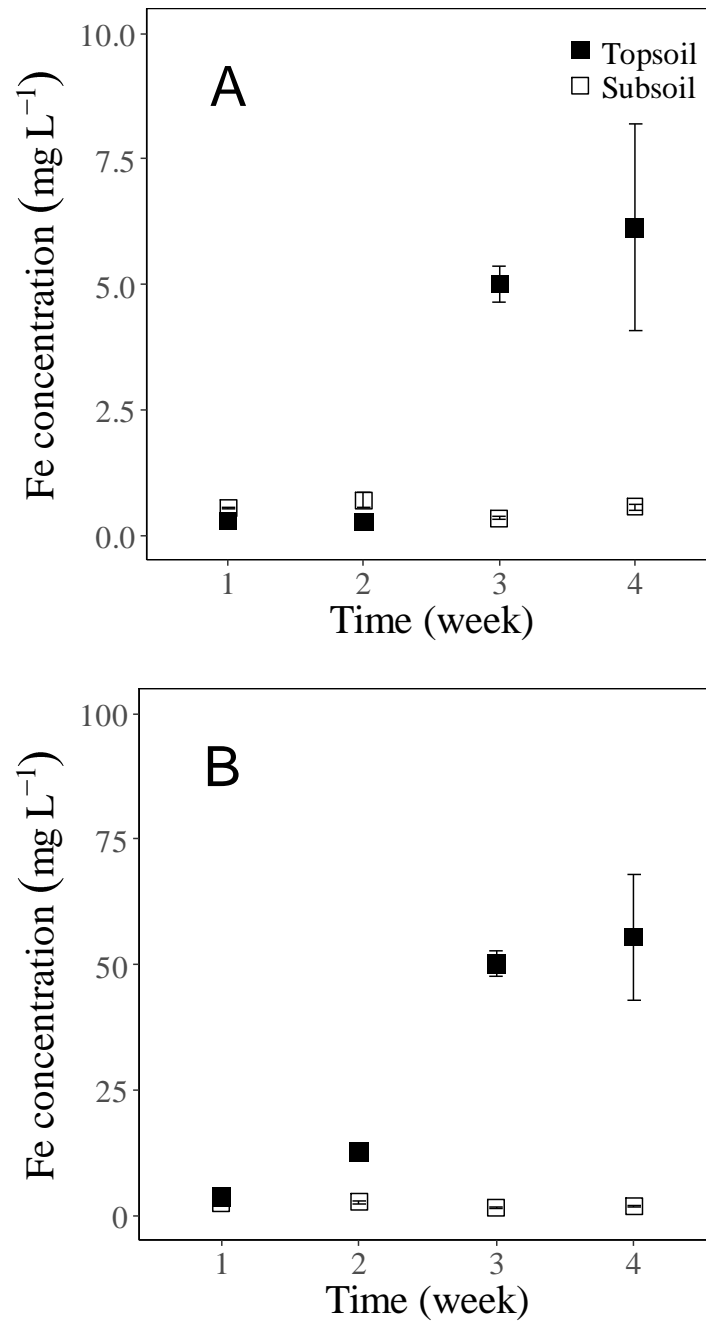


Fig. 6 Variation in mean ( $\pm$  standard error) Fe concentration in soil solution with incubation time in (A) arable and (B) woodland soils.

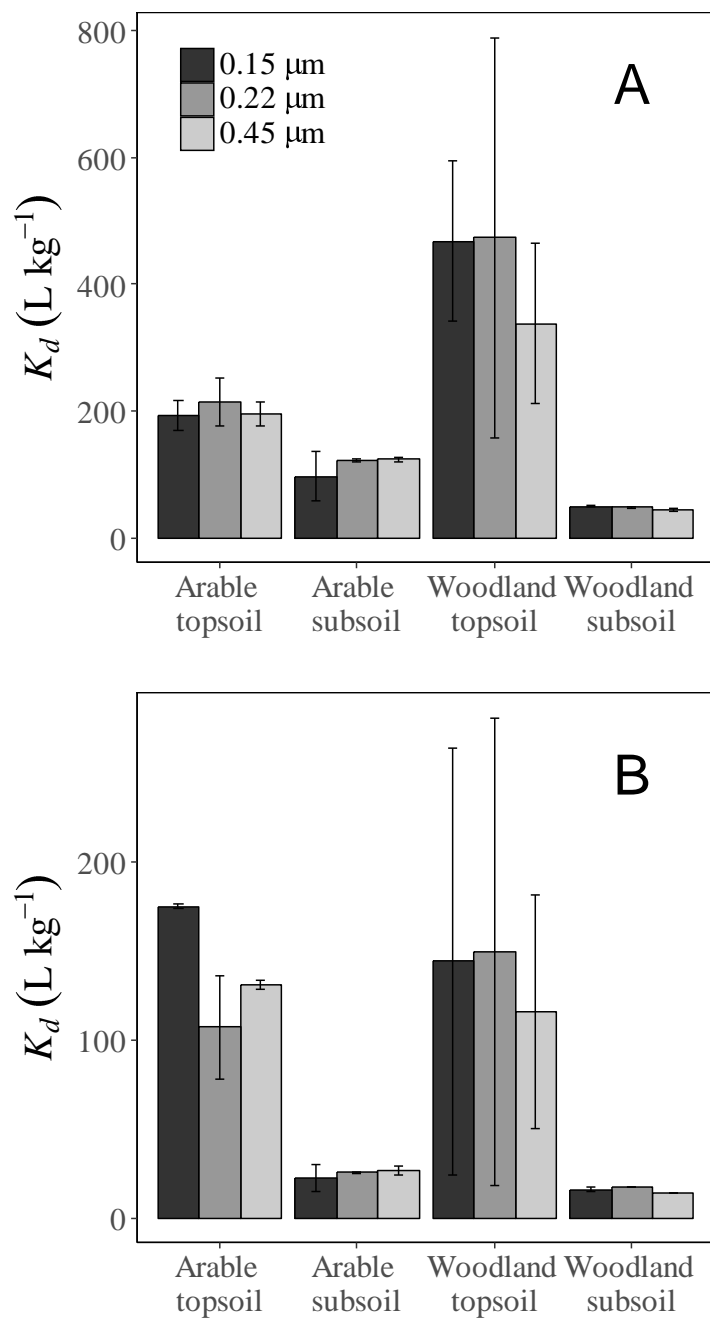


Fig. 7 Variation in mean ( $\pm$  standard error) desorption  $K_d$  values between 0.45  $\mu\text{m}$  0.22  $\mu\text{m}$  and 0.15  $\mu\text{m}$  filtrates for (A) Se and (B) I.