

Effects of moisture content and redox potential on in situ K_d values for radioiodine in soil

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Abstract

The soil solid–liquid distribution coefficient (K_d) value is of great significance in understanding and modelling the environmental behaviour of soil contaminants. For many years, the batch sorption technique has been used for the determination of such values. Here, we propose an alternative ‘mini-column’ approach in which somewhat more realistic soil conditions are maintained. In particular, this approach allows for determination of radionuclide K_d values under realistic soil moisture contents and in a system in which time-dependent processes such as changes in redox potential can take place. Data obtained for radioactive iodine (a key radionuclide in the consideration of radioactive waste disposal) are presented and indicate that soil moisture content, particularly in conjunction with soil redox potential (through water-logging of the soil), has a marked effect on measured K_d values. The results indicate the advantages and potential usefulness of the mini-column approach in assessing the environmental behaviour of radioactive, and other, soil contaminants.

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1. Introduction

The modelling of contaminant behaviour in the biosphere depends on reliable measurements of contaminant-specific parameter values. One of the most important of these parameters is the soil solid–liquid distribution coefficient, or K_d value, because this determines the potential for contaminant mobility

(leaching and plant uptake) within the soil–plant system. K_d is normally calculated as the ratio of soil solid phase concentration (per kg of soil) to soil solution phase concentration (per l of solution) (Eq. (1)). However, for particularly poorly sorbed contaminants, an alternative equation should be used in instances in which analytical constraints lead to the measured ‘solid-phase’ concentration actually representing both solid and solution phases (i.e. a total concentration). Clearly, the greater is the solution phase concentration in this case, the greater will be this inaccuracy, and overestimation of the K_d value

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will result. This alternative K_d equation should therefore first subtract the solution phase concentration from the total concentration in order to determine the true solid phase concentration. This can be achieved if the volumetric moisture content and bulk density of the soil are known (Eq. (2)). In either case, a low K_d value indicates a low degree of soil sorption and, potentially, high mobility. Conversely, a high K_d value indicates a high affinity for the soil solid phase (low mobility). One of the main advantages of the K_d approach in assessing the solubility of a contaminant is that, for a given soil, it essentially derives a single value which can then, for example, be readily used in computer modelling of the environmental behaviour of that contaminant.

$$K_d = S_d/S_n \quad (1)$$

$$K_d = ((T\rho) - (\theta S_n))/\rho/S_n \quad (2)$$

where: K_d is soil solid-solution partition coefficient ($l\text{ kg}^{-1}$); S_d is solid phase concentration (per kg soil); S_n is solution phase concentration (per l solution); T is total soil concentration (solid+solution) (per kg soil); ρ is soil bulk density (kg l^{-1}); θ is soil volumetric moisture content (dimensionless fraction).

For soils, the K_d value of a contaminant is most often determined using the batch sorption method in which increasing quantities of the contaminant are added in an excess of solution to a fixed mass of soil. After a period of ‘equilibration’ the loss of the contaminant from the solution is taken as a measure of soil adsorption. The relationship between adsorbed concentration and the concentration remaining in solution is termed the adsorption isotherm. For a linear isotherm, its slope gives the K_d value for the system. Non-linear isotherms are usually described using the Langmuir or Freundlich equations to give the system K_d values. The batch approach has been widely used to determine the K_d values of a range of contaminants in soil systems, e.g. heavy metals (e.g. Christensen et al., 1996; Markiewicz-Patkowska et al., 2005; Serrano et al., 2005), pesticides (e.g. Nemeth-Konda et al., 2002; Cooke et al., 2004; Li et al., 2005) and radionuclides (e.g. Bird and Schwartz, 1996; Mollah and Ullah, 1998; Echevarria et al., 2003).

The K_d value represents the ‘net effect’ of multiple soil sorption processes acting upon the contaminant

(e.g. ion exchange, complexation, precipitation). However, this is not to say that the K_d value for a given contaminant in a given soil is a constant. Indeed, many dynamic soil variables may further affect solid-solution partitioning, e.g. pH, moisture content, biological activity and oxidation–reduction (redox) potential. Such variables should be taken into account if a meaningful K_d value is to be derived. In general, however, such variables are not taken into account, particularly by the classical batch sorption methods. These methods are carried out at soil/water ratios of, typically, 1:5 or 1:10 which bear little resemblance to natural soil moisture conditions (usually 1:1 or higher). It is unclear to what extent this large excess of solution in batch experiments adequately represents the conditions applying in true soil solution. In addition, the short ‘equilibration’ periods typically used in batch methods (often hours) is likely to preclude variation in potentially time-dependent parameters such as pH and redox potential.

An ideal approach to determining K_d values experimentally is one in which, (a) realistic soil moisture contents can be maintained; (b) time dependent changes in soil variables are allowed to take place; and (c) a representative sample of interstitial water can be removed periodically without causing major disturbance to the soil–water system. We have therefore developed a ‘mini-column’ experimental approach which aims to realise these criteria. This paper describes the design and implementation of the mini-columns and reports initial results obtained for radioactive iodine. An evaluation of the experimental approach is given by a direct comparison with a deliberately short-term ‘batch’ technique and by considering the results in the context of previous research on iodine behaviour in soils.

^{129}I is emitted from nuclear fuel reprocessing and waste solidification facilities (Robens and Aumann, 1988). It is also a potentially important component of intermediate-level radioactive waste since it has a long physical half-life (1.6×10^7 years). For these reasons it is a key radionuclide of interest to nuclear waste disposal agencies and, as a consequence, is currently the subject of much research (which generally uses either the short-lived gamma emitter ^{125}I , or the stable isotope ^{127}I , as a tracer for ^{129}I). Disposal of radioactive waste to a deep geological repository is designed to isolate the waste from the biosphere. However, it is

recognised that it is important to assess the potential for the migration of radionuclides from a repository into, and throughout, the biosphere.

The anionic nature of iodine suggests that its environmental significance may be high since it is unlikely to become strongly adsorbed onto soils. However, iodine behaviour in the environment is dependent upon prevailing redox conditions. Murumatsu and Yoshida (1999) reported that the valence states of the major iodine species in the environment are: iodide, I^- (-1); iodate, IO_3^- (+5); elemental iodine, I_2 (0); and methyl iodide, CH_3I (+1). Of these, iodide and iodate are the most commonly encountered in soils.

Iodine sorption behaviour in soils has been shown to be affected by a number of soil properties. For example, soil organic matter content serves as an important sink for iodine (Ashworth et al., 2003), and acid/base equilibria lead to an increased potential for iodine solubility at high pH (Schmitz and Aumann, 1995). Studies have shown that when soil microbial biomass is reduced, the sorption of iodine is reduced (Bunzl and Schimmack, 1988; Bird and Schwartz, 1996). In addition, the volatilisation of iodine, presumably as methyl iodide, has also been reported (Bostock et al., 2003).

The effects of variation in soil redox potential on the sorption behaviour of iodine have also been studied in some detail. For example, Muramatsu et al. (1996) studied the effects of waterlogging on the desorption of ^{125}I from soil and found that, following waterlogging, the redox potential decreased and led to the lower soil adsorption of ^{125}I . Similarly, Sheppard and Hawkins (1995) found lower soil-sorption of added ^{125}I under anoxic conditions than under oxic conditions. In studying the upward transport of ^{125}I from contaminated water tables in experimental soil columns, Ashworth et al. (2003) and Shaw et al. (2004) found that the radionuclide was poorly sorbed, and hence mobile, only within the saturated, anoxic, soil zone at the base of the columns. Sheppard and Motycka (1997) found that such redox-induced decreases in iodine sorption led to higher concentrations of iodine in plants grown on flooded soil. These results suggest that the reduced, iodide, species is more mobile in the soil–plant system than the oxidised, iodate, form and is likely to exhibit a lower K_d value (Fukui et al., 1996).

Control of the sorption behaviour of iodine via oxidation–reduction reactions is important in relation to the release of radioactive iodine from deep disposal sites where a range of redox conditions may be prevalent in the near-field environment. Furthermore, migration of radioactive iodine across the anoxic/oxic boundary imposed by the water table would be required in order for it to reach the surface soils. Therefore, in order to carry out a meaningful risk assessment, K_d values determined in both anoxic and oxic conditions are required. Determination of such K_d values was the specific experimental objective of the work described here.

2. Materials and methods

2.1. Mini-column construction

A mini-column was constructed using commercially available, opaque plastic fittings (Marley Plumbing and Drainage, UK) assembled using epoxy resin which ensured that all joints and seals were water tight. The column had internal dimensions of 15 cm × 5 cm. A 3 mm diameter hole was drilled through the sidewall of the column at half the column height. A platinum electrode (redox probe) was made up using a 10 cm length of insulated copper wire attached to a 1.5 cm length of platinum wire using an insulated aluminium crimp-connector. Epoxy resin was used around the exposed ends of the crimp-connector to prevent the inner metal components becoming wet and corroded, when placed into the soil. The probe was then placed against the inner wall of the column with the copper wire running through the hole in the column sidewall, and the hole around the wire being sealed with epoxy resin. A 3 mm hole was also drilled into the centre of the base of the column (through the screw-on end cap). Through this hole a ‘Rhizon’ hollow fibre soil moisture sampler (Eijkelkamp, Netherlands) was inserted vertically so that the entire porous section (length 10 cm) was within the column. This was also glued into place with epoxy resin. A 1 cm hole was drilled into the centre of the top of the column (through the screw-on end cap). Into this hole was fitted and glued a 1 cm diameter tube to allow access for the addition of water and for a reference electrode. Six such columns were constructed. A cut-

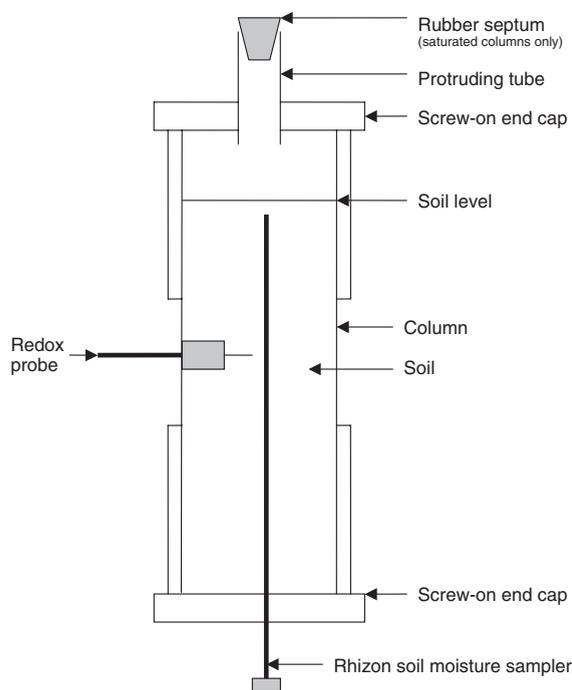


Fig. 1. Cut-away schematic diagram of a mini-column.

away schematic diagram of a complete mini-column is shown in Fig. 1.

2.2. Mini-column set-up

A sandy loam topsoil (Wicks series) collected from Silwood Park (Ascot, UK) was used to pack the columns. The soil was determined to have a pH in water of 4.3, an organic matter content (by loss-on-ignition) of 4.7% and to be non-stony. Its particle size distribution was determined (by dispersion and sedimentation) as 75% sand, 20% silt and 5% clay. For each column, 325 g of sieved (2 mm^2), but not ground, dry soil was weighed out into plastic bags. Three of these soil samples had their gravimetric moisture content adjusted to 25% by the addition of deionised water. The remaining three samples were saturated with deionised water; this equated to a gravimetric moisture content of 40%.

^{125}I was used as a surrogate for ^{129}I . ^{125}I has a physical half-life of around 60 days, decaying by electron capture with an energy of 0.186 MeV. ^{125}I was obtained from Amersham, UK as a carrier-free sodium iodide form. To each soil sample, a 1 ml

addition of ^{125}I containing solution (1.5 kBq) was made and mixed into the soil by manipulation by hand. Triplicate samples of soil were taken from each bag for the determination of initial specific activity. These analyses indicated that the coefficient of variation between the three samples was less than 10% in each case. Therefore, it was assumed that the soil was homogenous with respect to ^{125}I activity. The soils were then packed into the columns to a depth of 12.5 cm, producing an equivalent dry bulk density of 1.3 g cm^{-3} , before the upper end cap was replaced. In the 40% moisture content columns, standing water was present at the soil surface indicating that the soil was saturated. All columns were then weighed and the masses recorded. A rubber bung was placed into the 1 cm diameter tube on the top of the saturated columns in order to limit the entry of atmospheric oxygen to the column since the aim was to produce anoxic conditions in these columns. Because these tubes were made of clear plastic, partial light penetration to the soil surface was possible. The columns were then placed within a controlled environment room with a daytime (18 h) temperature of $20 \text{ }^\circ\text{C}$ and a nighttime (6 h) temperature of $15 \text{ }^\circ\text{C}$. Relative humidity was controlled at 70%.

2.3. Mini-column implementation

The experiment ran for 49 days. On days 1, 4, 7, 10, 14, 21, 28, 35, 42 and 49, a soil solution sample was removed from each column. This was achieved by attaching a syringe needle to the external end of the hollow fibre sampler and then pushing the needle into a vacutainer (BD Vacutainer Systems, UK). The negative pressure within the vacutainer (-50 to -60 kPa) resulted in the slow extraction of a 3 ml sample of soil solution through the hollow fibre sampler. This sample was retained for analysis. Following the removal of solution samples, columns were re-weighed and deionised water added to the soil to bring the columns back up to their initial mass (i.e. the moisture contents were maintained gravimetrically). In general, only the volume of water removed by the soil solution sampling was required to reinstate the desired soil moisture content, indicating that evaporative losses from the surfaces of the mini-columns were small. On the days on which solution samples were taken a measurement of the soil redox potential was also taken by

inserting a calomel reference electrode into the soil through the 1 cm diameter tube in the top of the columns and connecting it, via a high impedance voltmeter, to the platinum electrode. The mV reading was then added to 250 mV (the electrical potential of the reference electrode) to give the soil redox potential.

2.4. Batch experiment

For comparative purposes, the same sandy loam soil which was used in the mini-columns was also used to determine the adsorption behaviour of ^{125}I in a simple, short-term batch experiment. No attempt was made to control the conditions of this experiment (e.g. ionic strength, pH, redox potential). Similar experiments are often used for the estimation of contaminant K_d values because they are quick and easy to carry out.

Twenty milliliters of ^{125}I -containing solution was added to triplicate 4 g samples of air-dried soil. Several ^{125}I treatments were established viz: 8.7, 17.4, 43.5, 87.0, 174.0, 348.0 Bq. The samples were then placed on a slow end-over-end shaker for 2 h. At the start and end of this time, a platinum redox electrode and reference electrode (as described above) were inserted into several randomly selected samples to record the redox potentials. Following the 2 h shaking period, the samples were centrifuged at $2686 \times g$ for 15 min. The supernatant solution was then filtered through a Whatman cellulose nitrate 0.22 μm filter before a 5 ml subsample was taken for radiochemical

analysis. For each treatment, soil adsorption was determined by the difference in ^{125}I activity added initially and that remaining in the solution at the end of the experiment. An adsorption isotherm was prepared by plotting adsorbed specific activity (Bq kg^{-1}) against specific activity of the equilibrium solution (Bq l^{-1}). The slope of this linear relationship was taken as the system K_d value (l kg^{-1}).

2.5. Radiochemical analysis

^{125}I analyses of soils and soil solutions (mini-column experiment) and equilibrium solutions (batch experiment) were carried out using a solid-state scintillation gamma detector (EG and G Wallac 1282 Compugamma CS; Milton Keynes, UK) which makes use of a well-type sodium iodide crystal containing thallium. All analyses were carried out with reference to a primary standard of known initial ^{125}I activity, to allow for the conversion of counts per minute (cpm) to Bq. All ^{125}I data were decay corrected to the initial date of the experiment.

2.6. Non-radiochemical analysis

Soil solutions extracted from the mini-columns on days 1 and 49 were also analysed for nitrate and sulphate using a Dionex DX500 ion chromatography system with a Dionex AS11 column and a mobile phase of 6 mM sodium hydroxide. Determination of these ions was considered useful because they are

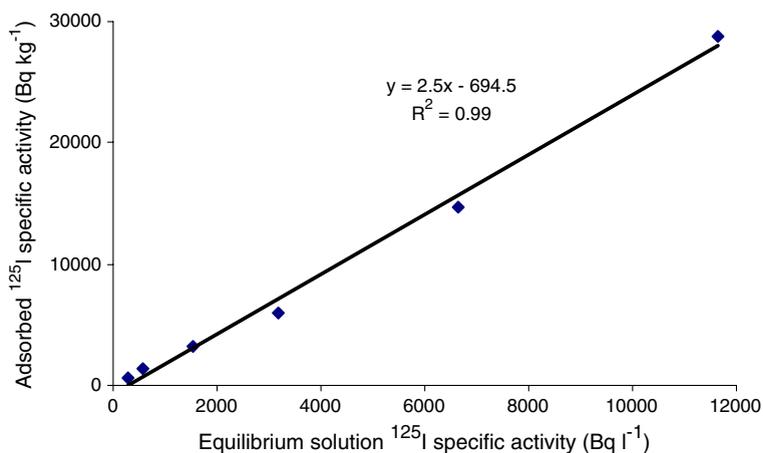


Fig. 2. Soil adsorption isotherm for ^{125}I .

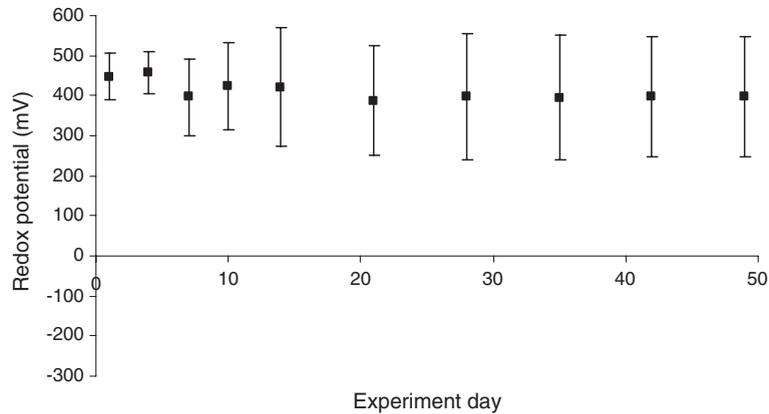


Fig. 3. Mean (± 1 standard deviation) redox potential values in the 25% moisture content columns over the course of the experiment.

indicators of soil redox status. Reduction of nitrate to nitrite occurs as soil becomes anoxic, whilst strong anoxia is characterised by the reduction of sulphate to sulphide (Sposito, 1989). Thus, solution concentrations of nitrate and sulphate over the course of the experiment could be used as redox-dependent indicators to corroborate the direct measurements of redox potential.

3. Results

Over the course of the batch sorption experiment, the soil samples remained oxic (with redox potentials between 300 and 400 mV). The adsorption isotherm resulting from the batch experiment is shown in Fig. 2. The slope of this relationship gives the K_d value for iodine in this system as 2.5 l kg^{-1} .

In the mini-column experiment, the 25% moisture content treatment led to oxic conditions (around 400 mV) being maintained over the course of the experiment (Fig. 3). However, in the 40% moisture content columns, whereas similarly oxic conditions were prevalent over the first 30 days of the experiment, after this time the redox potential began to fall, reaching -100 mV by the end of the experiment (Fig. 4). From Fig. 5, it is evident that in the drier columns neither nitrate nor sulphate concentrations decreased significantly between the start and end of the experiment. However, in the saturated columns, nitrate concentration decreased by around 60% between the start and end of the experiment.

K_d values were determined for all columns on the various sampling occasions using Eq. (2) by substituting specific activity (Bq kg^{-1} or Bq l^{-1}) for concentration. ‘Total’ specific activity of the soil was

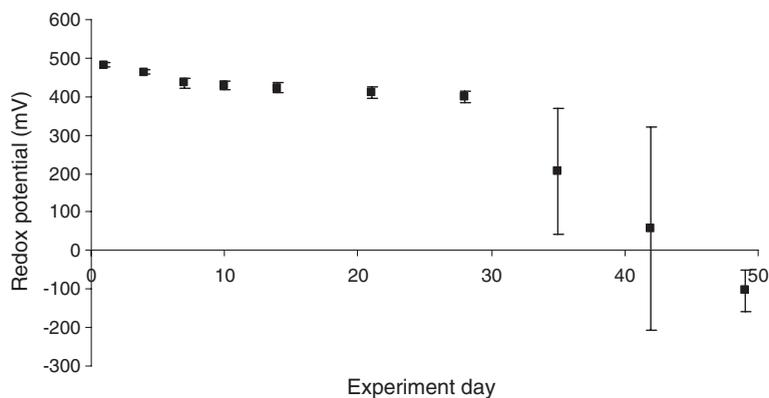


Fig. 4. Mean (± 1 standard deviation) redox potential values in the 40% moisture content mini-columns over the course of the experiment.

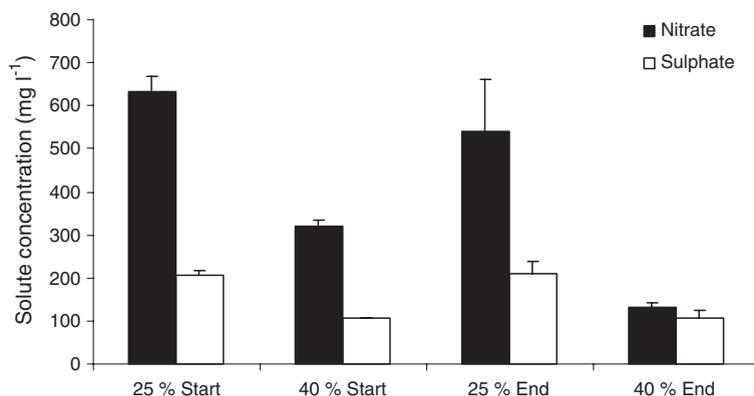


Fig. 5. Mean (± 1 standard deviation) nitrate and sulphate concentrations in the soil solutions extracted from the mini-columns at the start (day 1) and end (day 49) of the experiment.

taken as the initial specific activity measured in each of the soils before packing into the columns. K_d values over the course of the experiment are shown in Fig. 6. Over the first 2 weeks of the experiment, K_d values were below 1 l kg^{-1} in both treatments, indicating a relatively low degree of iodine sorption onto the soil. More specifically, over this period mean K_d values tended to be slightly lower in the 25% moisture content soils than in the 40% moisture content soils (although at day 14 almost identical mean values were observed). Whilst in both treatments, the K_d value tended to increase with time, this increase was much greater in the drier treatment; particularly after 3 weeks. By the end of the experimental period, K_d values in the drier columns had increased to, and

stabilised at, around 7 l kg^{-1} . The increase in K_d value in the saturated columns was somewhat smaller, to a maximum of approximately 2 l kg^{-1} .

4. Discussion

In contrast to the batch sorption experiment, saturation of the mini-column soil clearly led to a significant change in the redox status of the soil over time (Figs. 3 and 4). The relatively low redox potentials recorded in the saturated soils are typical of anoxic soils (Sposito, 1989). In addition, the results from the nitrate and sulphate analyses of the soil solutions at the start and end of the experiment (Fig. 5) offer a

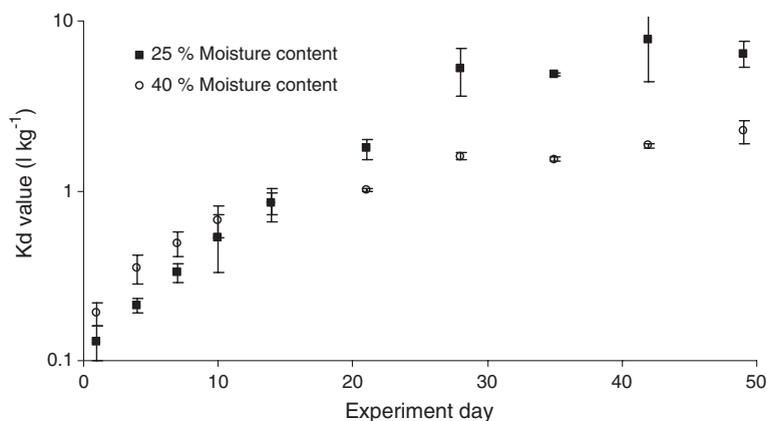


Fig. 6. Mean (± 1 standard deviation) ^{125}I K_d values in the 25% and 40% moisture content mini-columns over the course of the experiment (note log scale).

further insight into the redox chemistry of the soils. These suggest that, due to saturation, the redox status of the soil was such that nitrate was reduced to nitrite. However, the lack of a decrease in sulphate concentrations over the course of the experiment indicates that the redox potential was not sufficiently depressed to bring about sulphate reduction to sulphide. From these data, it is evident that the higher, saturated, moisture content brought about the partial reduction of the soil. This was likely to have been caused by the oxygen initially present within the soil being used up by microbial respiration over the first 30 days of the experiment. In contrast to the situation in the non-saturated columns, diffusion of atmospheric oxygen into the soil was reduced because the pore spaces were water-filled and the rubber bungs placed into the holes in the tops of the saturated columns prevented replenishment of oxygen in the small atmospheric headspace above the soil.

Because the effects of time dependent parameters are likely to be limited over the initial period of the experiment, the fact that K_d values were slightly lower in the 25% moisture content soils than in the 40% moisture content soils over the first 2 weeks of the experiment (Fig. 6) suggests that the prevailing moisture content rapidly affected K_d values. The data indicate that at the lower moisture content, a higher specific activity of ^{125}I was present in the soil solution (i.e. a lower K_d value was observed). This is likely to be due, at least to some extent, to dilution of soluble ^{125}I at higher moisture contents.

Although determination of the K_d value in the batch sorption experiment was carried out using a deliberately short contact time, it serves as a useful comparison to the data derived from the mini-column experiment. In particular, it allows for some of the potential problems associated with short-term batch experiments to be highlighted. For example, the observation that soil moisture content appeared to have a marked effect on K_d value in the mini-column experiment has significant implications for the usefulness of batch techniques which use low soil/moisture ratios, possibly resulting in lower solute concentrations and overestimates of K_d value. Indeed, this appears to be the case in the present work, as the K_d value determined here by the batch technique using a soil/solution ratio of 1:5 (Fig. 2) was greater than the initial K_d values observed in the mini-columns. Interestingly,

this effect of moisture content on soluble ion concentrations can also be seen in the nitrate and sulphate data (Fig. 5). For example, at the start of the experiment, when no redox-induced effect on ion concentrations would be expected, soil with 40% moisture content exhibited soil solution concentrations of both nitrate and sulphate which were lower than in the drier treatment.

The fact that K_d values generally increased over the course of the experiment, illustrates the importance of contact time between iodine and the soil. This raises questions over the reliability of K_d values determined using batch techniques over short time periods. For example, in an oxic system, the current mini-column work suggests that a K_d value determined after 1 day may be around 50 times lower than a K_d determined after around 40–50 days. This is probably due to the establishment of a time-dependent equilibrium between the iodine and the soil. In assessing environmental fate, the behaviour of a contaminant in equilibrium with its environment is often of primary interest. This result suggests that using a K_d value derived from short-term experiments can result in an overestimation of iodine solubility. Again, this appears to be borne out by the results from the batch experiment in which the short contact time (2 h) led to a much lower K_d value than was observed in the mini-columns at the end of the experiment (although this difference is offset by the effect of moisture content, as described above).

Differences in the magnitude of the time-dependent increases in K_d value between the two moisture treatments are thought to be a result of the observed trends in redox potential. The relationship between these two variables is shown in Fig. 7. The data suggest that the falling redox potential in the saturated treatment maintained iodine solubility much more effectively than in the drier treatment. This should be considered in the context of iodine speciation. Of the two main inorganic species of iodine likely to exist in soil solution, the oxic (iodate) form is thought to be more strongly adsorbed than the reduced (iodide) form (Fukui et al., 1996). Thus, in the saturated treatment, as redox potential fell, K_d value was apparently prevented from increasing as significantly as it did in the drier columns due to the chemical reduction of iodate to iodide.

It is useful to compare K_d values determined for ^{125}I in the present work with those previously reported

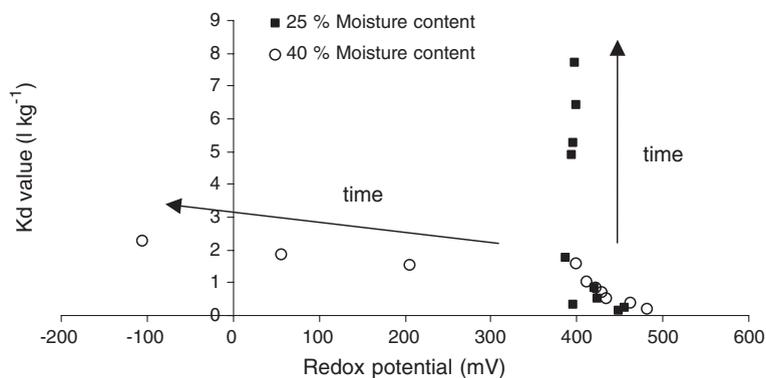


Fig. 7. Relationship between redox potentials and ^{125}I K_d values in the 25% and 40% moisture content mini-columns.

by other workers. A number of K_d values from batch studies using sandy soils and sediments (i.e. the same texture as the soil used in the present study) are available from the literature. For example, Bird and Schwartz (1996) reported average values ranging from 0.1 to 0.5 l kg^{-1} (the range of values depending on sediment to water ratio) for a sandy sediment under oxic conditions and with an equilibration period of 48 h. Fukui et al. (1996) found average values of 2.2–4.0 l kg^{-1} for iodide and 4.2–20 l kg^{-1} for iodate (the range of values depending on ambient temperature) for a fine sand and using a 14-day equilibration period. Bors et al. (1991) found K_d values of between 5 and 55 l kg^{-1} (an inverse relationship between temperature and K_d was noted) for a podzol (84% sand) using an equilibration period of at least 8 days.

A few compendia values of iodine K_d for sandy soils are also available. Sheppard and Thibault (1990) reported a range of K_d values for iodine ranging from 0.04 to 81 l kg^{-1} . I.A.E.A. (1994) reported a range of values, based on those of Sheppard and Thibault (1990), of 0.01 to 85 l kg^{-1} . Both of these studies reported a geometric mean value of 1 l kg^{-1} . In reviewing a range of literature sources, Sheppard et al. (2002) recommended a geometric mean K_d value for sandy soils of 8 l kg^{-1} . However, the overall range of literature K_d values found for sandy soils by these workers was large (0.23–695 l kg^{-1}). In the current study, mean K_d values ranged from 0.13 to 7.7 l kg^{-1} in the dry (oxic) soils, and from 0.19 to 2.3 l kg^{-1} in the saturated (anoxic soils). These values tend to be at the lower end of the range of literature values but seem consistent with geometric mean compendia values.

Whilst it is noted that the mini-column approach is still far removed from natural (dynamic) soil conditions, its advantage, as compared with the batch approach, seems to be that it allows for in situ K_d values to be readily determined in relation to time-dependent processes (e.g. for both oxic and anoxic conditions), and under realistic soil moisture contents. It should be noted of course that batch experiments can be carried out in a way which attempts to address these issues. For example, the contact time between the contaminant and the soil can be increased. Although only a short contact time was used here, often batch studies are carried out over longer periods in order to determine the time at which an apparent equilibrium between the solid and solution phases (with respect to the contaminant) is reached. Nevertheless, this period seems seldom long enough for time dependent processes to take place, e.g. a lowering of redox potential in the saturated mini-columns was not observed until after 30 days. Therefore, in general, literature contaminant K_d values are reported only for oxic environments. The relatively few studies that also consider anoxic environments (typically by carrying out batch experiments under an artificial N_2 environment) rarely quantify the redox potential of the system. From a modelling perspective, it is therefore difficult to know which K_d values are appropriate for oxic and, particularly, anoxic environments, based on current data.

5. Conclusions

This work has illustrated potential uncertainties associated with the use of simple batch techniques

to determine contaminant K_d values in soils. Firstly, the batch technique necessitates an excess of solution to be added to the soil. This is unrepresentative of the true soil solution since it has been shown here that soil moisture content affects ion concentrations within the solution phase. The use of 'Rhizon' hollow fibre soil moisture samplers in the mini-columns allows the removal of soil solution at realistic soil moisture contents. For this reason, it is considered that these samplers provide a more reliable representation, with regard to ion concentrations, of the soil solution and, hence, allow a more reliable calculation of K_d value.

The second potential limitation of a short-term batch technique is that it perhaps does not sufficiently allow for time dependent processes to affect the partitioning of the contaminant. In these experiments, time-dependent sorption rates induced by changes in redox potential were not adequately accounted for using the, albeit short-term, batch approach. This was particularly applicable to the study of iodine in this work, since iodine sorption was found to be markedly decreased under anoxic conditions.

Using the mini-column approach equilibrium ^{125}I K_d values of around 2 and 7 l kg^{-1} were observed for anoxic and oxic conditions respectively, indicating that iodine within oxic environments is less mobile and, presumably, less bio-available than in anoxic environments. In the context of the risk assessment of radioactive waste disposal, this suggests that ^{129}I from contaminated groundwater is likely to be relatively poorly sorbed within the saturated soil zone (below the water table) and that its transport to the soil surface by evapotranspiration is likely to be slowed within the oxic soil region due to greater sorption. Similarly, the present study indicates that soil-surface applied ^{129}I (e.g. from contaminated irrigation water) is likely to experience a greater degree of sorption within the soil. These processes are likely to restrict the transfer of ^{129}I from soil to plants, and hence to the food chain.

The mini-column approach seems to provide a useful system for determining in situ K_d values under more realistic soil conditions than can be realised using a batch sorption approach. The system could easily be adapted for the study of a wide range of soil contaminants (e.g. heavy metals, pesticides, PAH, PCB, pharmaceuticals, nutrients) under a

wider range of soil conditions (e.g. differing pH, organic matter content, soil texture, microbial activity/populations). The mini-column method could, therefore, provide an improved approach to assist in our understanding and modelling of contaminant fate within the environment.

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