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Soil migration, plant uptake and volatilisation of radio-selenium from a contaminated water table

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Abstract

The properties of ^{79}Se make it of likely potential importance in safety studies for geological disposal of radioactive wastes. Despite a substantial literature on toxic and nutritional aspects of selenium in the environment little consideration has been given to the behaviour of radioactive selenium and its potential transfer from a radioactive waste repository to the biosphere. Column experiments (15 × 50 cm), using a sandy loam soil, indicated that the upwards migration of ^{75}Se (as a surrogate for ^{79}Se) from a contaminated water table was dependent upon the redox status of the soil. Low redox conditions within the water table strongly limited upwards ^{75}Se soil migration, presumably due to the immobilisation of reduced Se species. Under natural conditions, ^{79}Se from a radioactive waste repository is therefore likely to accumulate at considerable depth. As a consequence, its absence from the rooting zone is likely to limit its transfer into plants. Nevertheless, the column experiments indicated that when an overlap between roots and soil contamination occurs, uptake into the plant is observed. Quantification of ^{75}Se volatilisation from the column surfaces suggested that this is a significant pathway by which ^{79}Se may move either directly from soil to the atmosphere, or from soil to plants and then to the atmosphere.

Keywords: ^{79}Se; ^{75}Se; Radioactive waste disposal; Selenium speciation; Redox potential; Soil columns

1. Introduction

Selenium-79 is formed as a product of ^{235}U fission within the reactor core of nuclear power plants. The physical half life of ^{79}Se is uncertain. Originally thought to be around 6.5×10^4 years (ICRP, 1983), more recent estimates are around 1.13×10^6 years (Chu et al., 1999). The re-evaluation of its half-life has led to an increase in the significance of ^{79}Se in the context of radioactive waste disposal. One potential option for the disposal of radioactive waste is burial within a deep geological repository. The potential for release of radionuclides from geological repositories over extended time periods, for example under future climate scenarios, is currently a subject for research. The behaviour of potentially released radionuclides also requires research effort in order to quantify the risks associated with the geological disposal option. The fact that ^{79}Se is likely to be found predominantly in anionic (potentially poorly-sorbed)

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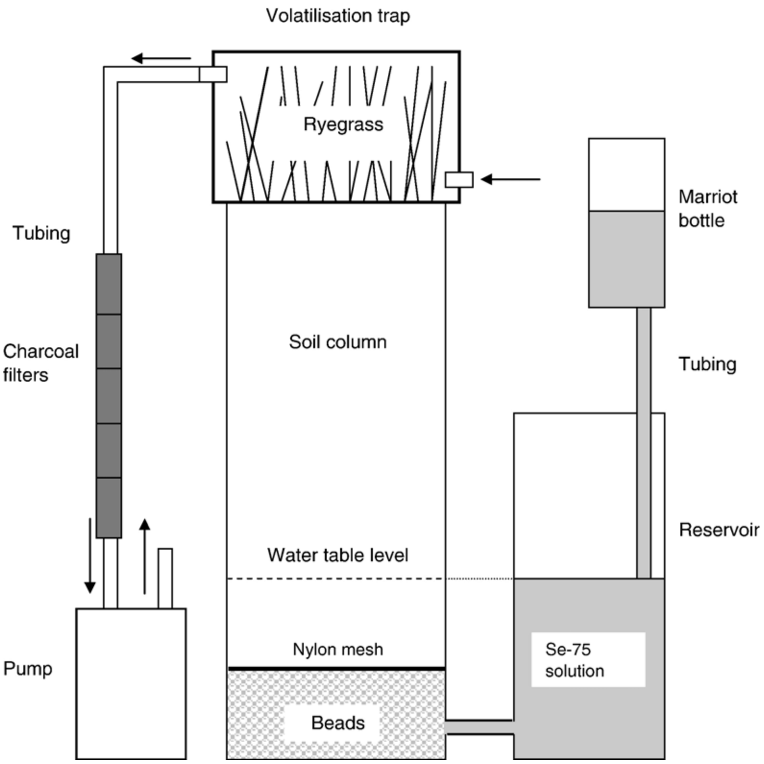

Fig. 1. Schematic diagram of a functioning soil column.

form in rock at depth, coupled with its re-evaluated, relatively long, half-life means that it now needs to be included in such a risk assessment. One of the pathways of interest in this regard is contamination of groundwater followed by migration of radionuclides through soil and into the rooting zone of vegetation.

Inorganic Se potentially exists as one of four species in soil, viz: selenates (Se VI), selenites (Se IV), elemental Se (Se 0) and selenides (Se-II). The behaviour of Se in soils is dependent on a number of factors, including the pH and chemical and mineralogical composition of the soil, microbial interactions and the nature of adsorbing surfaces (Neal, 1995). However, perhaps the most important influence on Se behaviour is the soil redox potential (Eh). Generally, the more reducing (low redox potential) the soil conditions, the more immobile Se becomes. The four inorganic Se species thus become increasingly mobile in the order selenide < elemental Se < selenite < selenate. K_d values for Se have been published by IAEA (1994) and these are based on estimates by Sheppard and Thibault (1990). These values are 150, 490, 740 and 1800 L kg^{-1} for sand, loam, clay and organic soils, respectively. Thorne et al. (2001) recommended Se K_d values of 18 L kg^{-1} for brown acidic soil, 35 L kg^{-1} for colluvial soil, 70 L kg^{-1} for brown rendzina and 170 L kg^{-1} for organic soil. Nakamaru et al. (2005) found K_d values from 12 to 1060 (mean 315) L kg^{-1} for a wide range of soils. Overall, literature K_d values for Se tend to be relatively high, suggesting a high degree of immobilisation, even under the presumably oxic conditions at which they were determined (i.e. primarily in batch equilibration experiments). Given a high degree of immobilisation in soil, the degree of uptake of Se from the soil solution into plant roots would be expected to be relatively low. Coughtrey et al. (1983) gave soil–plant concentration ratios (dry mass basis) of 5 for selenite-amended soil and 30 for selenate-amended soil. Data from Saas et al. (1982) indicate that higher concentration ratios than this can occur, whereas Johnsson (1991) found concentration ratios of the order of 1 (on a dry mass plant basis). Kloke et al. (1984) provided a range of soil–plant transfer coefficients for Se from 0.1 to 10. Thorne et al. (2001) recommended a transfer coefficient of 1.0 (fresh weight plant/dry weight soil) with an uncertainty range of 0.1 to 30. A further aspect of the fate of Se within the environment is its potential to volatilise. It has been demonstrated that the microbial methylation of Se, by both aerobic and anaerobic bacteria and fungi, can result in the generation of volatile methyl selenide species (Masscheleyn et al., 1991). In addition, methyl selenides can be synthesised by higher plants, a process exploited in order to phyto-remediate Se contaminated land (Berken et al., 2002). Thus, there appears to be a potential for biogenic volatilisation of Se from both soils and plants.

This paper describes a soil column experiment which aimed to quantify the soil–plant–air relations of radio-selenium introduced via a near-surface water table. In such a controlled system, the effects of hydrological, chemical and biological variables on the behaviour of the radio-selenium could be taken into account. More specifically, the following working hypotheses were tested:

a) Upwards soil migration of radio-selenium introduced via a water table will be low due to the formation of reduced, relatively immobile, Se species in the anoxic soil zone.
b) Plant uptake of radio-selenium will be low due to a lack of overlap between the contaminated soil (immobilised at depth) and the plant roots (predominantly at the surface).
c) Volatile Se species will be formed and emitted from the soil and plant surfaces.

2. Materials and methods

The general design and establishment of the soil columns have been described previously by Ashworth and Shaw (2005) and so only the most significant details of the design are described here. PVC columns (50 × 15 cm) were packed with a screened (1 cm^2), homogenised, field moist sandy loam topsoil (Wicks series) at a uniform bulk density of around 1 g cm^{-3}. The soil was collected from Imperial College's field station at Silwood Park (Berkshire, UK) and was determined to have a pH in water of 4.3, a loss-on-ignition value 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. Deionised water was used to establish fixed-depth water tables (at 45 cm from the soil surface) in the soil columns. The general design of the experimental soil columns is shown in Fig. 1.

Thirteen columns were prepared for destructive sampling at either 3, 6 or 9 months. The various treatments are shown in Table 1. Both vegetated (with perennial ryegrass, *Lolium perenne*) and non-vegetated (control) columns were used and selected columns also had volatilisation traps fitted. Volatilisation traps (15 × 15 cm) were made from Perspex and 'capped' the column surface. Air was pumped continuously across the column surface, and through five charcoal filters (Tube 32, ORBO, Poole, UK). In the three vegetated, 9-month columns, platinum probes (to determine oxidation–reduction, or 'redox', potential), time domain reflectometry (TDR) probes (to determine in-situ soil moisture content) and hollow fibre ('Rhizon') soil moisture samplers were inserted into the soil at various soil depths (as described by Ashworth and Shaw, 2006). Once set up, the columns were randomly positioned in a controlled environment room under a daily cycle of 18 h light (at 20 °C) and 6 h darkness (at 15 °C) per day. The relative humidity within the room was maintained at 70%. After 15 days, the water tables were dosed with ^{75}Se (as a surrogate for ^{79}Se) obtained in a selenite, carrier-free form from Isotope Products, Germany. The initial activity concentration of the water tables was 20 Bq mL^{-1}.

Table 1
Summary of the soil column treatments

Time to destructive sampling	Perennial ryegrass cover	Volatilisation trap	TDR, redox, and soil solution samplers	Number of columns
3 months	Yes	No	No	3
3 months	No	No	No	1
3 months	No	Yes	No	1
6 months	Yes	No	No	3
9 months	Yes	No	Yes	3
9 months	Yes	Yes	No	2

On a weekly basis, measurement of in-situ redox potential and moisture content was carried out at the various soil depths. On a monthly basis, samples of soil solution were extracted, the ryegrass was cut to a height of 5 cm above the soil surface, and charcoal filters were removed. These samples were analysed for ^{75}Se. At the time intervals shown in Table 1, soil columns were destructively sampled in order to determine the distribution of ^{75}Se activity throughout the column system.

All ^{75}Se analysis was carried out using a solid-state scintillation gamma detector (LKB Wallac 1282 Compugamma CS; Milton Keynes, UK) which makes use of a well-type NaI(Tl) crystal. All analyses were carried out with reference to a 0.1 mL sample of ^{75}Se of known activity (3600 Bq), to allow the conversion of counts per minute (cpm) to Bq. Samples were counted initially for 1000 s but this was increased if low cpm values, with high counting errors, were obtained. For most samples, 1σ counting errors were typically less than 10 %. All ^{75}Se data were decay corrected to the start of the experiment and so results from different sampling/analysis times are directly comparable.

3. Results

Mean total solution influxes into the 3-, 6- and 9-month columns (without volatilisation traps), as measured by losses from the Marriot bottles, are shown in Table 2. Influxes increased over time although a lack of vegetation led to markedly lower overall influxes in the 3-month columns. Storage of water within the soil profile followed

Table 2
Mean and standard deviation (where applicable) of total ryegrass biomass, total ryegrass ^{75}Se uptake, and total solution influx to columns

	3 months non-vegetated	3 months vegetated	6 months vegetated	9 months vegetated
Solution influx (mL)	2.5	4.0 (1.4)	9.7 (0.5)	12.4 (2.0)
Ryegrass fresh weight biomass (g)	–	24.7 (16.3)	58.7 (2.9)	57.8 (17.1)
Ryegrass ^{75}Se uptake (Bq)	–	8.6 (5.5)	25.8 (4.7)	27.0 (9.3)

an expected trend. From around 3 weeks after the establishment of the water table, a steady-state moisture profile was observed. This was characterised by saturated soil in the bottom 10 cm of the columns. Above this, the soil became progressively drier with decreasing depth. The soil moisture profile would be expected to influence directly the profile of redox potential within the soil columns. Thus, the saturated conditions at the bottom of the columns led to the development, over the first 20 days, of anoxic conditions (−100 to −200 mV) in this region. Above this, redox potentials were maintained at oxic levels towards the soil surface. A steady-state redox profile throughout the entire column was observed from around 6 weeks after the establishment of the water table. Comparable trends in soil moisture content and redox potential have been previously observed in very similar column experiments (Ashworth et al., 2003; Ashworth and Shaw, 2006).

Profiles of mean ^{75}Se activity concentrations within the soil are shown in Fig. 2 for the 3-, 6- and 9-month soil columns (without volatilisation traps). Generally similar profiles were observed at each sampling time. Taking into account the log scale, it is apparent that on each sampling occasion, the bulk of ^{75}Se was retained in the bottom-most (48–50 cm) soil layer. Indeed, on average, 86 (S.D.=3)% of the total soil ^{75}Se was found in this layer. Nevertheless, some migration above this layer was observed and activity was consistently detected through to the 35–40 cm depth layer at all sampling times. In the 6 and 9-month columns, further migration, above the 35–40 cm layer was observed. Most notably, in the 0–5 cm layer (i.e. at the soil surface) low, but detectable, activity concentrations were found. By comparing the profile for the 3-month non-vegetated treatment with that of the 3-month vegetated treatment, it can be seen that the presence of vegetation did not appear to have a large effect on the pattern of upwards transport of the ^{75}Se. However, the observed soil activity concentrations in some of the layers were lower in the non-vegetated treatment than in the vegetated treatment.

Mean ^{75}Se activity concentrations of soil solutions extracted at various column depths throughout the experiment are shown in Fig. 3. The lowermost sampler (52.5 cm) was inserted into the polythene bead substrate and, in the absence of a ‘loss’ of activity (e.g. via sorption onto the plastic components used to construct the column system, or precipitation due to low redox potential) the activity concentration of the solution extracted through this sampler should reflect that of the Marriot bottle-reservoir input solution (20 Bq mL^{-1}). At 1 month, the activity concentration in the bead substrate solution was around 0.7 Bq mL^{-1} and thereafter tended to decline over time, reaching 0.25 Bq mL^{-1} in Month 9. This indicates that a significant ‘loss’ of ^{75}Se did take place in this region and this is considered below. The bead substrate solution should therefore be considered as the ‘input’ solution to the soil. As such, the fact that between 30% (at Month 1) and 60% (at Month 9) of the activity concentration value in the bead substrate solution was recorded in the soil solution at 47.5 cm indicates that further immobilisation of ^{75}Se, once within the soil, took place. In addition, it is clear that the activity concentrations of the soil solutions declined

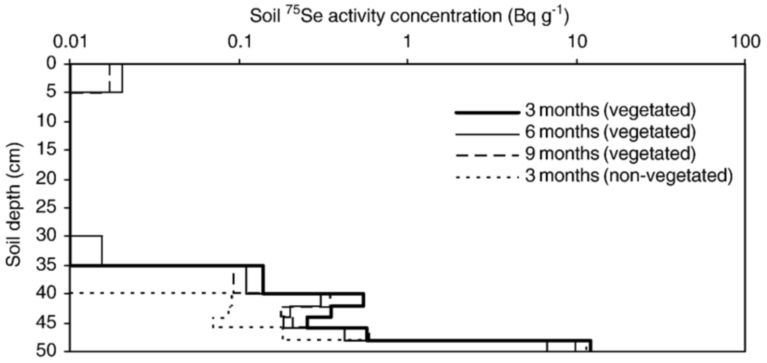

Fig. 2. Mean soil ^{75}Se activity concentration profiles for the 3, 6 and 9-month soil columns, without volatilisation traps.

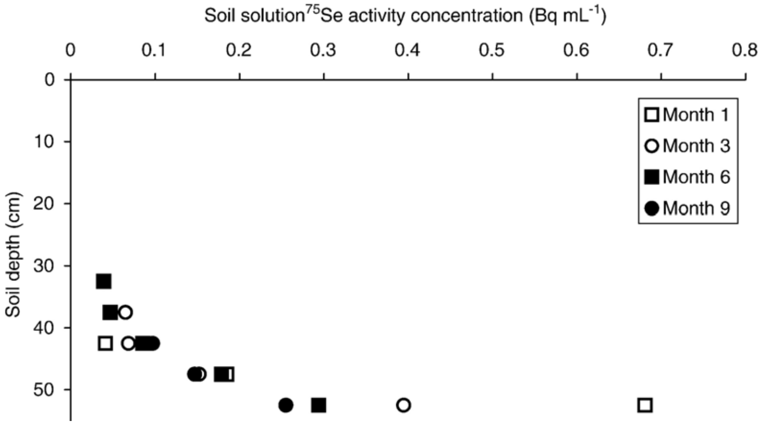

Fig. 3. Mean soil solution ^{75}Se activity concentration profiles.

with decreasing depth, which is consistent with the observed total soil activity concentrations. Using both solid and solution phase activity concentrations, it was possible to calculate in-situ K_d values for ^{75}Se at the base of the columns. Mean values were 5 (S.D. = 2) and 46 (S.D. = 19) L kg^{-1}, at 42.5 and 47.5 cm respectively.

On a month by month basis, the activity concentrations and the biomass yields of the ryegrass were not well related (Fig. 4). In Table 2 the *total* ryegrass biomass, *total* ^{75}Se uptake, and *total* solution influxes of the columns are given. Linear regression of these data for the 9 vegetated columns without volatilisation traps showed that total ryegrass biomass yield from a column was strongly and positively correlated ($r^2 = 0.92$; $p < 0.001$) with the total ^{75}Se ryegrass uptake from that column. Similarly, the total ryegrass uptake of ^{75}Se from

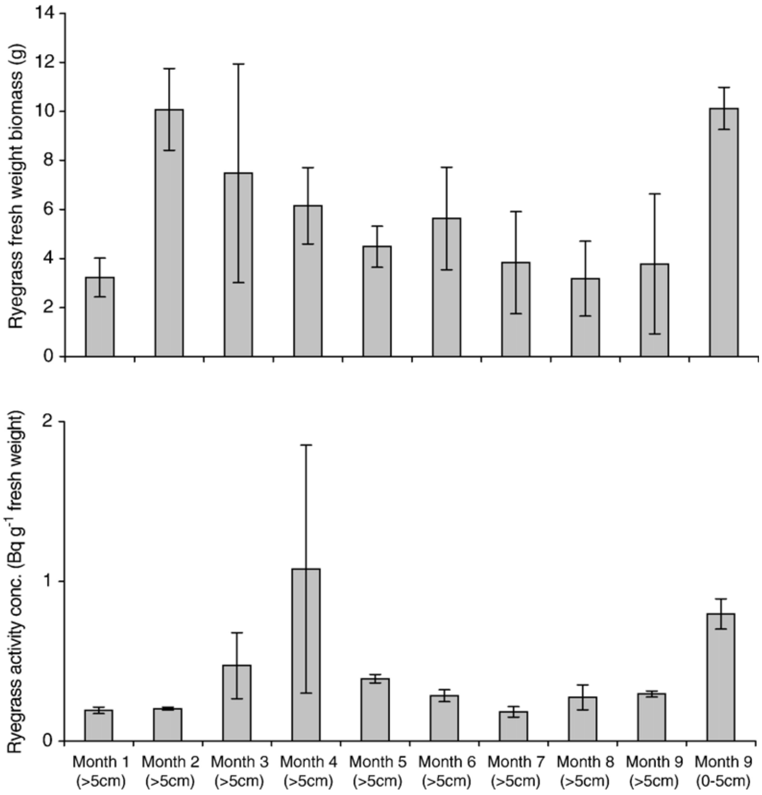

Fig. 4. Mean and standard deviation monthly perennial ryegrass biomass and ^{75}Se activity concentrations for the vegetated 9-month columns (without volatilisation traps).

a column was positively correlated ($r^2 = 0.87$; $p < 0.01$) with the total solution influx into that column. In addition, total ryegrass biomass was also positively and strongly ($r^2 = 0.82$; $p < 0.01$) correlated with total solution influx to the columns.

Throughout much of the soil profile, little difference in ryegrass root density between the 3-, 6-, and 9-month columns was observed. Greatest difference was observed in the top 5 cm of soil where mean root density (dry weight root/dry weight soil) increased from 1.08 (S.D. = 1.07) g kg^{-1} at 3 months, to 1.95 (S.D. = 0.23) g kg^{-1} at 6 months, and 2.64 (S.D. = 0.55) g kg^{-1} at 9 months. Root density generally decreased with increasing depth, with the 48–50 cm layer having values of 0.11 (S.D. = 0.09), 0.11 (S.D. = 0.02) and 0.08 (S.D. = 0.02) g kg^{-1} for the 3-, 6- and 9-month columns respectively, indicating that relatively few ryegrass roots penetrated to this depth. However, these roots were found to contain ^{75}Se, with activity concentrations for the 3-, 6- and 9-month columns of 48 (S.D. = 24), 591 (S.D. = 159) and 495 (S.D. = 160) Bq g^{-1} (dry root basis), respectively. Above this layer, only in the 9-month columns was any ^{75}Se activity found in the root material, and then only in the 46–48 cm soil layer (activity concentration 216 (S.D. = 63) Bq g^{-1}). Soil–plant transfer factors, weighted to account for the non-uniform distribution of roots throughout the profile, were calculated according to the expression given by Wadey et al. (2001). These averaged 208 (S.D. = 111) in the 3-month columns, 136 (S.D. = 53) in the 6-month columns, and 124 (S.D. = 48) in the 9-month columns (equivalent dry weight basis, assuming a dry:fresh ratio of 1:10).

Selenium-75 activities were measured on all five of the charcoal filters at each sampling time, indicating that not all of the volatilised ^{75}Se was trapped. Nevertheless, a trapping efficiency of greater than 80% using the 5 traps in series was estimated. Mean volatilisation rates for the vegetated (over 9 months) and non-vegetated (over 3 months) columns are shown in Fig. 5. In the vegetated columns, these ranged from around 5.1 to 15.4 Bq m^2 day^{-1}, and in the non-vegetated columns, from around 3.8 to 5.5 Bq m^2 day^{-1}. No clearly discernible time-wise trend was seen.

Table 3
Mean percentage recovery of ^{75}Se from the system components

Fate	%
Soil	7
Ryegrass	0.04
Volatilisation	0.1
Plastics	62
Residual solutions	21
Total	90

The total activity input to each column was compared with the recovered activity at the time of destructive sampling. Mean percentage recovery of ^{75}Se activity from the various column components is shown in Table 3. As alluded to earlier, large quantities of activity were recovered from the plastic surfaces within the system (average 62%), primarily the bead substrate. However, sufficient activity reached the soil to allow reliable ^{75}Se measurements for soil, solutions, plant tissues and headspace air. Percentages recovered from the ryegrass and lost by volatilisation were relatively low. Overall system recoveries averaged 90% (range 72–102%).

4. Discussion

Throughout the experiment, hydrological flow was maintained from the Marriot bottles, through the soil columns and into the atmosphere above the plant and soil surfaces, as indicated by the development of ‘steady-state’ soil moisture content profiles, coupled with increasing water influxes over time. Thus, rather than water simply being stored in the soil columns in a

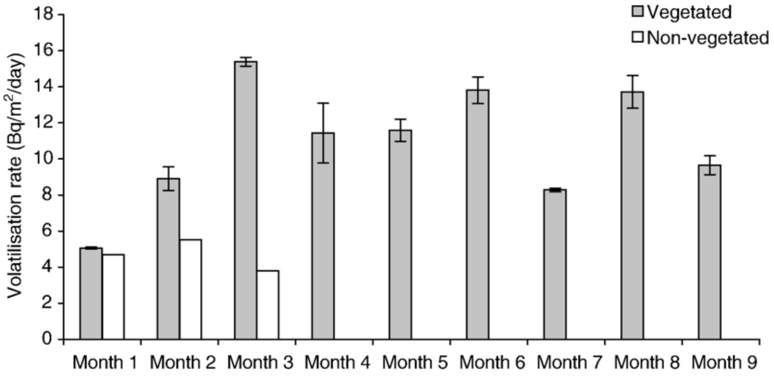

Fig. 5. Mean and standard deviation (where applicable) monthly ^{75}Se volatilisation rates from the soil columns, with, and without, vegetation cover.

static condition, water influx into the columns was balanced by loss in the form of evapotranspiration from the column surface. In virtually identical experiments, ^{36}Cl was seen to migrate through 50 cm soil columns, from a contaminated water table at 45 cm depth, within 6 months (even with the relatively low total solution influx of 3500 mL) (Ashworth and Shaw, 2006). $^{36}Cl^-$ is often considered to be an almost ideal tracer for the movement of water, due to its extremely low degree of sorption in soils. Our previous observations of ^{36}Cl therefore indicate that advective–diffusive processes have the *potential* to transport contaminants from the water table to the soil surface. However, in the present experiment ^{75}Se migration was limited to the bottom 10–15 cm (and particularly the bottom 2 cm) of soil. Clearly, therefore, the ^{75}Se became strongly immobilised within the soil, suggesting that soil chemistry exerted a greater control on ^{75}Se migration than hydrology. To underline this observation, the total solution influx into the 9-month columns was around three times greater than into the 3-month columns, yet the difference in upwards migration of ^{75}Se between these two sets of columns was minor.

Selenium behaviour in soils is thought to be controlled by its redox-dependent speciation. The order of decreasing solubility of the four inorganic selenium species is given by Neal (1995) as selenate > selenite > elemental Se > selenide. According to the redox potential (−130 to −230 mV) and pH (6.8 to 7.6) observed at the base of the soil columns (47.5 cm depth), the Eh/pH stability diagram for Se suggests the dominance of elemental Se and selenide species. Such species are known to be relatively insoluble, with selenides, in particular, forming solid phase precipitates in soils (Seby et al., 1998). Thus under reduced soil conditions, such as those observed at the base of the soil columns, the less soluble forms of Se would be expected to dominate, limiting upward migration. Such a process may also explain the high activities found to be associated with the polythene bead substrate and the consequentially low activity concentrations of its solution, since the redox potential within this region often fell to anoxic levels (down to −157 mV). Nevertheless, because the ^{75}Se often reached the 35–40 cm depth it is clear that some upward migration through the soil did take place within the first 3 months of the experiment (i.e. it was not all adsorbed in the lowermost, 48–50 cm, layer). This would appear to indicate a kinetic effect in which the immobilisation of ^{75}Se may have increased with time, at least partly in response to the developing anoxic conditions at the base of the columns over the early stages of the experiment.

The tendency for ^{75}Se to become immobilised, and generally show limited upwards migration, is borne out by the relatively high in-situ K_d values at the very base of the columns (within the water table). The lower K_d values observed in the 40–44 cm soil layer (directly above the water table) indicate a lower degree of immobilisation and may have been due to the influence of oxygen diffusion into this zone, thereby favouring the formation of more soluble Se species (e.g. selenates and selenites). However, it should be noted that marked differences in redox potentials between the soil below the water table and that directly above it were not measured. The measured K_d values for the (sandy loam) soil used in the experiment reported here seem comparable with the range of values (1.8 to 180 L kg^{-1}) for sandy soils given by Thorne et al. (2001).

The absence of vegetation greatly reduced the influx of solution to the 3-month columns. This may have been the cause of the generally lower soil activity concentrations observed in the non-vegetated columns, since less ^{75}Se activity was drawn into these columns. However, marked differences in the extent of ^{75}Se migration within the bottom 10–15 cm of the soil columns were not seen when comparing the vegetated and non-vegetated columns, again suggesting that hydrological flux into the columns was not significant in determining upwards migration. Nevertheless, it is considered that the presence of vegetation may have been important in the apparent transportation of ^{75}Se to the soil surface. If this had taken place via soil diffusion–advection processes, a presence of ^{75}Se throughout the soil profile would be expected. As noted by Wadey et al. (1994), the vertical migration of highly sorbed radionuclides by physicochemical solute transport mechanisms is likely to be augmented by root absorption in the subsoil and upward translocation within vascular tissues. Results for the ryegrass analysis (discussed below) clearly showed that ^{75}Se was taken up into plant tissues. Two possible mechanisms exist by which plant-incorporated ^{75}Se may have been released back into the surface soil. The first is via senescence of leaf tissue onto the soil, followed by incorporation into the soil matrix (humification). The second is via exudation from roots within the surface soil. Given the relatively long period of time required for the operation of the first mechanism the second possibility is most likely on the time scale of the experiment. Although ^{75}Se was only detected in ryegrass roots removed from the 46–50 cm layers of soil, its presence in the above ground biomass indicates its movement through the entire plant and, hence, a potential for this soil surface-exudation mechanism. The ability of plants to exude substances including organic acids (Nye and Tinker, 1977) and radiocaesium (Zhu et al., 2000) into the rhizosphere has been documented. Given the apparent propensity for several organic compounds within plants to complex with Se (Petersen et al., 1981), it seems possible that Se could be exuded in this form. The reason that this apparently only occurred at the soil surface may have been due to the much greater density of roots in this region.

Ryegrass biomass appeared to play a key role in controlling solution influx (via transpiration) and, hence, plant uptake of ^{75}Se. Nevertheless, the activity concentrations of the ryegrass were low, with the total uptake of ^{75}Se by the ryegrass over 9 months representing just 0.39 (S.D. = 0.25)% of the total soil activity measured at 9 months. This low degree of uptake was presumably a result of the general lack of overlap between the contaminated soil at depth and the dominant fraction of ryegrass roots within the top 5 cm of the columns. This has also been observed for ^{125}I (Ashworth et al., 2003; Ashworth and Shaw, 2006) and ^{95m}Tc (Ashworth and Shaw, 2005) in our previous soil column experiments; both radionuclides undergoing redox dependent immobilisation below the dominant rooting zone. The most notable feature of ryegrass ^{75}Se activity concentrations is the presence of activity after just 1 month. This suggests that roots quickly penetrated the soil and were able to absorb the ^{75}Se towards the base of the columns. Given that ryegrass roots would not be expected to tolerate anoxic soil, it seems likely that the observed penetration of roots throughout the entire soil profile occurred prior to the development of the anoxic conditions around the water table. Under such conditions the ^{75}Se entering the soil column would be expected to be relatively soluble, and, hence, more available for plant uptake than it became once anoxic conditions developed. As anoxic conditions developed, reduced bioavailability of the ^{75}Se, coupled with a potentially reduced root uptake efficiency (for example through death of roots in the anoxic soil) is likely to have limited uptake of ^{75}Se into the ryegrass. Continued uptake over the course of the experiment is therefore likely to have been a result of uptake from less strongly reduced soil where roots could survive and ^{75}Se solubility would be greater. The weighted soil–plant transfer factors determined for the soil columns were relatively high compared to the literature values of Johnsson (1991) (around 1) and Kloke et al. (1984) (from 0.1 to 10). However, if the transfer factors from the columns are considered on a fresh weight plant basis, (i.e. 12.4 to 20.8), they fall within the 0.1 to 30 range (also expressed on a fresh weight plant material basis) reported by Thorne et al. (2001).

Guo et al. (2001) reported that a significant fraction of Se in soils and sediments could be lost through volatilisation of methyl selenide and detectable concentrations of atmospheric Se were found by Chau and Wong (1986). In terms of a ^{75}Se loss mechanism from the columns, volatilisation appeared to be a more significant process than plant uptake. In the vegetated columns fitted with volatilisation traps, the total emission of ^{75}Se over the 9-month period represented 3.8 (S.D. = 0.1)% of the total soil activity measured at 9 months, i.e. around an order of magnitude greater than the uptake into the ryegrass over this period. In terms of volatilisation from the soil, the fact that the ^{75}Se was predominantly within the bottom 10–15 cm of the soil column would suggest that it was within this anoxic zone that production of volatile Se species took place. As noted by Masscheleyn et al. (1991), the presence of anoxic conditions may be significant in bringing about the formation of the volatile methyl selenide species. Volatile Se species formed at the base of the soil columns must then have passed upwards through the soil pores to be released from the top of the column. However, the data also clearly indicate the importance of the vegetation in relation to ^{75}Se volatilisation from the columns, with up to 75% (in month 3) of the total volatile loss occurring through the plant. This importance seemed to increase with time, presumably due to the time-dependant exploitation of the soil by the roots. The synthesis of methyl selenide within plants, and its volatilisation from leaf surfaces has been reported by Berken et al. (2002), and provides a likely explanation for the observed volatilisation from the ryegrass.

5. Conclusions

Although extrapolation from a laboratory-based study to the real world is always problematic, the study of radionuclide transfer from groundwater to the biosphere requires such an approach since real world experiments of this nature cannot be easily, nor often ethically, carried out. Most problematic in extrapolating from this experiment to the real world is in accounting for the influence of environmental variables, such as precipitation. Nevertheless, it is thought likely that such variables would not have significantly affected the results of the experiment since the dominant factor in determining the migration behaviour of the ^{75}Se was chemical rather than hydrological. Redox chemistry exerted a strong control through the chemical reduction of Se to highly immobilised forms (probably elemental Se and selenides) in the anoxic zone of soil at the base of the columns. This suggests that the transfer of ^{79}Se from a radioactive waste repository towards the biosphere would be severely limited due to reducing conditions within the saturated zone extending from host rock to subsoil.

Transfer from soil to plants was shown to be a potential pathway by which ^{79}Se may be transported to the soil surface. This mechanism relies on an overlap occurring between plant roots and contaminated subsoil, which, under natural conditions, may not be realised due to the expectation that the ^{79}Se would become immobilised at considerable depth (i.e. below the rooting zone). However, should radio-selenium be sufficiently mobile to enter the rooting zone, the experimental results suggest that transfer to plants may be relatively high (weighted transfer factors of around 120 to 200 observed). Measurement of volatile ^{75}Se at the surface of the columns also indicates a potential pathway by which ^{79}Se may move either directly from soil to the atmosphere, or, more significantly, from soil to plants and then to the atmosphere. Selenium-79 should therefore be considered in any potential risk assessment of the geospheric disposal of radioactive waste. Part of such a risk assessment should include a modelling approach in order to consider the long term (thousands of years) behaviour of ^{79}Se, since such time scales cannot be considered experimentally. This experiment provides detailed information on the processes that should be represented in such models.

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