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Radionuclide Transport Above a Near-Surface Water Table: IV. Soil Migration and Crop Uptake of Chlorine-36 and Technetium-99, 1990 to 1993

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ABSTRACT

Vertical distributions of ^{36}Cl and ^{99}Tc are presented from deep and shallow lysimeters above artificially controlled water tables for a 4-yr experiment from 1990 to 1993. Activity concentration profiles were all measured in late summer when a winter wheat (*Triticum aestivum* L. cv. Pastiche) crop was harvested. After harvest, activity concentrations in different organs of the crop were determined and crop uptake quantified as both an inventory ratio (IR) and a transfer factor (TF_w), weighted to account for differential root and radionuclide distributions within the soil profile. Vertical distributions of radionuclides, crop roots within the soil, and IR and TF_w values were each subjected to analysis of variance to estimate the individual and combined effects of soil depth and the year of the experiment on the results obtained. Chlorine-36 and ^{99}Tc exhibited highly significant variations in activity concentrations with soil depth and from year to year, indicating considerable physical mobility of both radionuclides. Soil-to-plant transfer was also high for both radionuclides compared with data obtained for gamma-emitting radionuclides. The IR values indicated that up to 40% of ^{36}Cl was incorporated in the crop's tissues at harvest, compared with a maximum of less than 1% for the less mobile gamma-emitting radionuclides. On the basis of the TF_w values determined, ^{36}Cl uptake by winter wheat exceeded ^{99}Tc uptake, indicating that ^{36}Cl is highly bioavailable. Factors controlling the migration and bioavailability of both ^{36}Cl and ^{99}Tc in soils are discussed.

The physical half-lives of ^{36}Cl and ^{99}Tc are long (3.01×10^5 and 2.0×10^5 yr, respectively) and they are expected to be mobile in both the geosphere and biosphere as both radionuclides exist within the environment predominantly in anionic forms (Sparkes and Long, 1988). Chlorine-36 is a significant radionuclide in the disposal of UK Intermediate Level Waste (Nirex, 1993, 1997, 2003) and Canadian spent fuel (Sheppard et al., 1996). These previously published studies show that soil-to-plant transfer of ^{36}Cl within the biosphere is an important factor in determining the calculated radiation dose to man some thousands of years or more after closure of a deep radioactive waste repository.

The four-year lysimeter experiment described in this paper was designed to investigate the upward migration of radionuclides in vegetated soils above near-surface ground water under conditions that were as natural as possible. Thus, ambient hydrological inputs and outputs were used in the experimental design, which is described in detail by Burne et al. (1994). This paper presents a summary of results obtained for ^{36}Cl and ^{99}Tc in the experiment, which was performed at Silwood Park (Ascot, southern England) from 1990 to 1993, inclusive, under the Nirex Safety Assessment Research Programme. Wadey et al. (2001) have previously presented summary results for gamma-emitting radionuclide migration and meteorological and hydrological data for the four years of the lysimeter experiment, as well as a summary of soil redox potentials within the lysimeter soil profiles over the latter half of the experiment.

In the second paper of this series, Wadey et al. (1994) reported on the dearth of quantitative information about soil-to-plant transfers of radionuclides in general following subsurface migration. For ^{99}Tc, much information relevant to surface contamination of soils was derived during the 1970s (Wildung et al., 1977) and 1980s (Grogan et al., 1987) and considerable steps were taken to understand the plant metabolism of this "artificial" element (Lembrechts et al., 1985; Lembrechts and Desmet, 1986, 1989). Some of this information was compiled by the International Union of Radioecologists (IUR) as part of a soil-to-plant transfer factor (TF) database (International Union of Radioecology, 1989) relating to the direct contamination of surface soils. Several of the contributions within the compilation of papers edited by Desmet and Myttenaere (1986) refer to the tendency of ^{99}Tc to exist in either the Tc^{VII} ($^{99}TcO_4^-$) or the Tc^{IV} ($^{99}TcO_2$) states within the environment, depending largely on redox conditions and the presence of natural complexing agents such as humic and fulvic acids. Most experiments addressing surface contamination of soils have involved the direct addition of $^{99}TcO_4^-$ to the soil: in this state ^{99}Tc behaves in a similar fashion to NO_3^- and is highly mobile and bioavailable (Echevarria et al., 1998). Accordingly, soil-to-plant transfer factors, the ratio between radionuclide activity concentrations in plant tissue and soil (usually expressed on a dry weight basis), are high (3.2×10^{-1} to 3.4×10^3), and are the largest values in the International Union of Radioecology database. The current experiment, however, involved the migration of both ^{99}Tc and ^{36}Cl from a highly reducing subsurface zone into an aerobic topsoil within a lysimeter. Under these conditions it was not certain whether previously published soil-to-plant transfer factors for ^{99}Tc would apply.

Data for soil migration and plant uptake of ^{36}Cl are almost completely absent from the literature. Coughtrey et al. (1983) reviewed the literature available for stable chlorine behavior in soils and plants and concluded that a high degree of soil-to-plant transfer would be expected (TF for stable Cl, expressed on a dry weight basis, was

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Abbreviations: IR, inventory ratio; LSC, liquid scintillation counting; TF, transfer factor; TF_w, weighted transfer factor; WMAC, weighted mean activity concentration.

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approximately 50). Furthermore, these authors noted that a "considerable removal of applied activity" of radiochlorine would be expected due to rapid uptake by plant roots. The estimated soil-to-plant TF of Coughtrey et al. (1983) was in good agreement with the later experimental findings of Sheppard et al. (1993), although these experimental determinations were made for stable chlorine and are not necessarily applicable to ^{36}Cl, with a concentration in soil that is likely to be several orders of magnitude lower than that of the stable element (although, if ^{36}Cl is well mixed with stable chlorine in the soil and is in the same chemical form, predominantly chloride, there should be negligible discrimination between them). Migration of ^{36}Cl from an underground nuclear test site has been reported by Ogard et al. (1988), who found that, as a result of anion exclusion, movement of $^{36}Cl^-$ in ground water was faster than ^3HHO, an effect that has also been observed in soil column experiments in our own laboratory (Lee, 1997). Hence, it was hypothesized that soil migration and crop uptake of both ^{36}Cl and ^{99}Tc would be substantially greater than observed for the radioisotopes of Cs, Co, and Na reported in the previous paper in this series (Wadey et al., 2001).

MATERIALS AND METHODS

The establishment, radiochemical dosing, and routine operation of the lysimeter system were described in detail by Burne et al. (1994). A brief summary of the experiment is given here. Two fixed water table heights were maintained in a total of eight lysimeters (i.e., four replicate lysimeters per water table "treatment") with each lysimeter having an area of 182 × 91 cm. The four replicate lysimeters per treatment had water table depths of 35 cm (shallow) or 65 cm (deep). The total soil depth in each lysimeter was 40 or 70 cm, respectively. A sandy loam (Eutric Cambisol; Tavernier, 1985) soil, derived from the Silwood Park estate, was present in all lysimeters. The soil was supported on a layer of geotextile material (Hy-Tex, Ashford, UK) above an inert substrate of polythene beads into which a cocktail of radionuclides could be introduced and circulated. Four successive crops of winter wheat were planted in the autumn of each year from 1989 to 1992 and allowed to grow to maturity before harvesting in the late summers of 1990 to 1993. Dosing of the lysimeter system with the radionuclide cocktail was performed in April or May of each year (Table 1). The radionuclides were added as $Na^{36}Cl$ and $NH_4{}^{99}TcO_4$, respectively. Consequently, the initial chemical forms of the two radionuclides when added to the artificial "ground water" of the lysimeter system were $^{36}Cl^-$ and $^{99}TcO_4^-$, the chloride and pertechnetate anions, respectively. It was expected that ^{36}Cl would remain as the $^{36}Cl^-$ anion and that ^{99}Tc would be subject to some degree of conversion between the $^{99}Tc^{VII}$ and $^{99}Tc^{IV}$ states according to the prevailing redox conditions in different parts of the lysimeters.

Sampling of Soil and Plant Material

Vertical core samples of soil were taken immediately after wheat harvest in late summer. Core samples, 3.8 cm in diameter, were taken with a commercial tube-type sampler (Eijkelkamp Agrisearch Equipment, Giesbeek, the Netherlands) down to the geotextile layer, which marks the base of the mineral soil within the lysimeters. All soil "depths" are therefore recorded as "height above geotextile" which, for the purpose of this experiment, is the ground water flow distance up from the geotextile, equivalent to soil depth reported in conventional experiments. The sample holes were packed with uncontaminated soil identical to that within the lysimeters. Cores were taken to the laboratory where they were quickly extruded and cut into depthwise segments; the lowest 10 cm of cores was divided into 2-cm segments whereas the remainder of each core was divided into 10-cm segments. This gave 8 depth samples for shallow lysimeters and 11 depth samples for deep lysimeters. Each depth sample was stored in a refrigerator at 4°C while awaiting radiochemical analysis.

Individual wheat plants were harvested by cutting the tillers approximately 2 cm above the soil surface, after which they were air-dried and divided into leaves, stems, chaff, and grain. From the 1992 harvest onward, the wheat ear was further divided to give a rachis and chaff sample. All samples were weighed and stored in a dry condition awaiting analysis.

Table 1. Total activities of beta-emitting radionuclides added to the Silwood Park lysimeter system from 1990 to 1993.

Year	^{36}Cl	^{99}Tc
	MBq	
1990	247	237
1991	32	32
1992	29	35
1993	32	32
Total	340	336

Beta Analysis of Soil and Plant Material

The ^{36}Cl and ^{99}Tc content of soil and plant samples was determined by liquid scintillation counting (LSC) using a 1219 Rackbeta Spectra Master liquid scintillation counter (Wallac/PerkinElmer, Wellesley, MA). The LSC was calibrated to allow dual counting of ^{36}Cl and ^{99}Tc. Radionuclides were obtained from either Amersham (Buckinghamshire, UK) or DuPont (Wilmington, DE).

Soil Analysis

A simple method was adopted to extract both radionuclides from the soil assuming that ^{36}Cl and ^{99}Tc were likely to be present predominantly in the Cl^- and TcO_4^- forms. A 10-g (fresh weight) subsample of soil was removed from each depth sample and placed in a 100-mL polythene centrifuge tube. Deionized water (70 mL) was added and the centrifuge tube was shaken for 2 h in an end-over-end shaker. The tubes were then centrifuged for 15 min in a bench centrifuge at 4000 rpm (2.0×10^3 N kg^{-1}). Fifty milliliters of the supernatant were decanted from each tube and placed in a 75-mL polystyrene container for concentration by freeze-drying. One hundred microliters of 1 *M* NaOH was added to increase the pH of the sample to >9, to prevent any loss of ^{36}Cl during freeze drying. On reaching dryness, the extracts were made up to a volume of 2 mL with deionized water and transferred to 6-mL centrifuge tubes for a further 15-min centrifugation at 4000 rpm, to remove any remaining sediment. One milliliter of the supernatant was then passed down a cation exchange column (1-cm diameter, 10-cm length, packed with Dowex 50W-X8[H] 100-200 mesh resin; Dow, Indianapolis, IN) with deionized water as the eluent. This step removed the (cationic) gamma-emitting radionuclides that were also present in the lysimeter soil and would otherwise have interfered with the analysis of ^{36}Cl and ^{99}Tc by LSC. Ten milliliters of eluent were collected from the cation exchange column in a scintillation vial. Twenty microliters of 1 *M* NaOH were added to each vial to increase the pH of the sample to a pH of >9. The samples were taken to dryness by freeze drying and then made up to 1 mL with de-

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ionized water and prepared for liquid scintillation counting by the addition of 10 mL of OptiPhase Hisafe II scintillation fluid (Wallac/PerkinElmer).

To correct for any loss of ^{36}Cl or ^{99}Tc during the sample preparation procedure, one standard for each soil core was produced from 50 mL of soil water extract and 70 Bq of each radionuclide. This standard was treated in the same way as water extracts taken directly from the soil core samples (i.e., subject to the freeze-drying and anion exchange procedures described above). Recovery from freshly spiked soil was 98% (^{36}Cl) and 95% (^{99}Tc) using the deionized water extraction method described here. Subsequent analyses have shown that some reduction in recovery of ^{36}Cl occurs in soils as a result of binding to organic materials (Lee et al., 2001).

Plant Analysis

To release ^{36}Cl and ^{99}Tc from wheat a 1-g sample was placed in a pear-shaped glass flask with 10 mL of 16 *M* HNO_3 and heated for 3 h from 90 to 120°C. The ^{36}Cl evolved was collected in a series of three absorption traps containing 5 *M* NaOH. The majority of the ^{36}Cl was collected in Trap 1, which contained 25 mL of 5 *M* NaOH at the start of the extraction. Traps 2 and 3 contained 4 mL of 5 *M* NaOH each. After 3 h, approximately 75% of the ^{36}Cl initially present in the wheat had been released from the sample and trapped. Heating was stopped and the splash head and absorption traps were dismantled. The final weight of solution in the traps was recorded before a 500-mg subsample was taken and placed in a scintillation vial with 10 mL of OptiPhase Hisafe III scintillation fluid (Wallac/PerkinElmer) for analysis by LSC.

The residue from the first step of the extraction contained ^{99}Tc and a mixture of the gamma-emitting radionuclides. In the second step of the extraction procedure, complete digestion of the wheat tissue occurred, resulting in a colorless solution that was passed through a cation exchange column to remove gamma-emitting radionuclides before beta analysis by LSC. The residue was evaporated in the pear-shaped flask at approximately 120°C until approximately 5 mL remained. Several additions of nitric acid, deionized water, and hydrogen peroxide were made as follows: 5 mL of 16 *M* HNO_3, 5 mL of H_2O, 5 mL of H_2O, 5 mL of 16 *M* HNO_3, 5 mL of H_2O_2, and finally 5 mL of H_2O with the residue heated until only 2 mL of solution remained in the flask. Between each addition, the residue was evaporated until approximately 5 mL remained. The volume was reduced further to approximately 2 mL before addition of hydrogen peroxide.

The residue, in a final volume of 2 mL, was passed through a cation exchange column (1 × 5 cm, packed with Dowex 50W-X8[H] 100-200 mesh resin). New resin was used for each residue sample and each was eluted with 20 mL of deionized water. The sample was collected from the column in 2 × 10-mL aliquots in preweighed scintillation vials. The weight of each residue aliquot was determined before a 500-mg subsample was taken from each and placed in a separate scintillation vial with 10 mL of OptiPhase Hisafe III scintillation fluid for analysis by LSC. The ^{99}Tc activities in each of the aliquots were determined separately and then summed to give the total activity in the original sample.

The yields of ^{36}Cl or ^{99}Tc (70–78%) were determined by the extraction of standards produced from nonactive wheat material spiked with known quantities of ^{36}Cl and ^{99}Tc, extracted under the same conditions as the samples. Radioactivity associated with the radionuclides was calculated as Bq kg^{-1} dry weight and is referred to within this paper as "activity concentration."

Root Distribution at Harvest

Root distributions within lysimeters were measured on a regular basis throughout the growing season, using a rigid endoscope as described by Burne et al. (1994).

Statistical Analysis

Data were subjected to a series of two- and three-way analyses of variance (ANOVA) based on the fixed treatment effects model (Sokal and Rohlf, 1969). The following variates were examined:

- soil activity concentration depth profiles (kBq kg^{-1})
- weighted mean soil activity concentrations (WMAC; kBq kg^{-1})
- soil-to-plant inventory ratios (IR; dimensionless)
- weighted soil-to-plant transfer factors (TF_w; dimensionless)

Each of these variates was approximately log-normally distributed, and the data were ln-transformed before analysis. This transformation produced approximately normally distributed data sets with homogeneous variances, two fundamental prerequisites for ANOVA (Sokal and Rohlf, 1969).

RESULTS

Radionuclide Distribution Profiles

The depth profiles of ^{36}Cl and ^{99}Tc activity concentrations are shown at each of the four annual harvest dates (Fig. 1 and 2). Chlorine-36 and ^{99}Tc were highly mobile and migrated rapidly from the region just above the water table (5 cm above the geotextile) to the surface. A sharp decrease in the activity concentration of ^{99}Tc is evident from the geotextile (0 cm) to a height of approximately 10 cm above the geotextile (Fig. 2). In both deep and shallow lysimeters the water table was fixed at 5 cm above the geotextile, so this region of decreasing concentration represents the highly reduced zone immediately above and below the water table. In the more oxic upper regions of the soil profile ^{99}Tc was distributed almost uniformly with height above the geotextile. A two-factor ANOVA was performed (Table 2), which confirmed that the differences in activity concentration of ^{36}Cl observed at different soil "heights" and from year to year were all significant for both deep and shallow lysimeters. Additionally, significant interaction was detected in the statistical analysis between "height" and year indicating that significant changes in the overall shapes of the ^{36}Cl profiles occurred over the course of the experiment in both deep and shallow lysimeters. Differences observed in the vertical distributions of ^{99}Tc activity concentration profiles in deep and shallow lysimeters and from year to year were significant, though interaction between these factors was not (Table 2).

Weighted Mean Activity Concentrations of Soil Profiles

The WMAC of a radionuclide within the soil profile can be calculated as follows:

$$\mathrm{WMAC} = \sum_{i=1}^{n} ([R]_i f_i)$$

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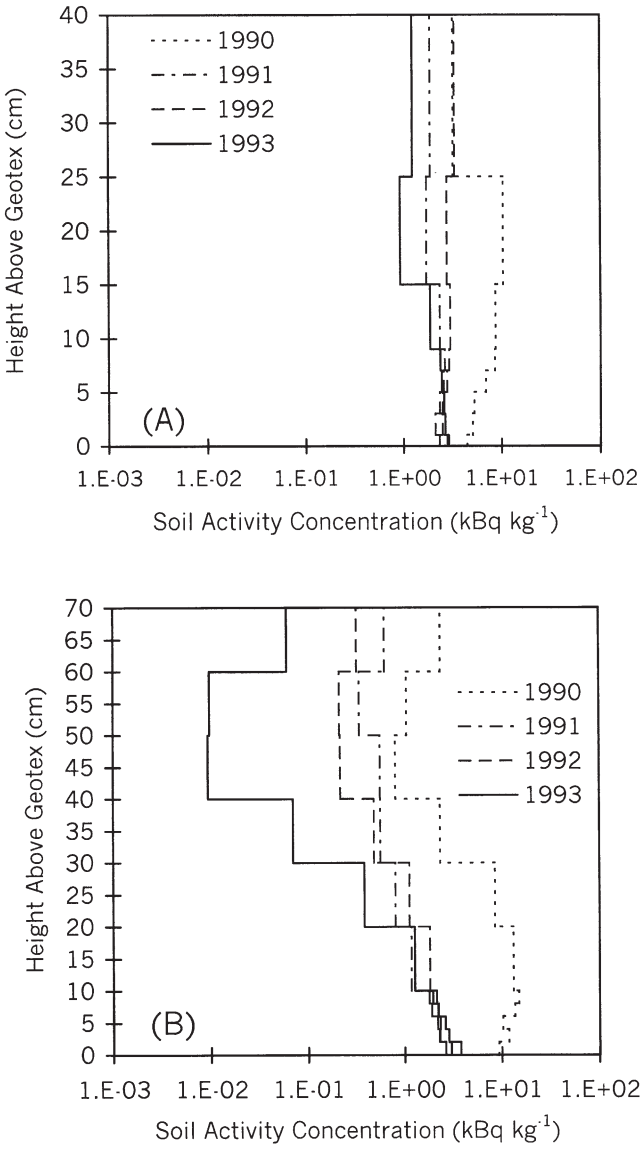

Fig. 1. Vertical distributions of ^{36}Cl activity concentrations in (A) shallow and (B) deep lysimeters from 1990 to 1993. The soil surface is located 40 and 70 cm above the geotextile material in the shallow and deep lysimeters, respectively.

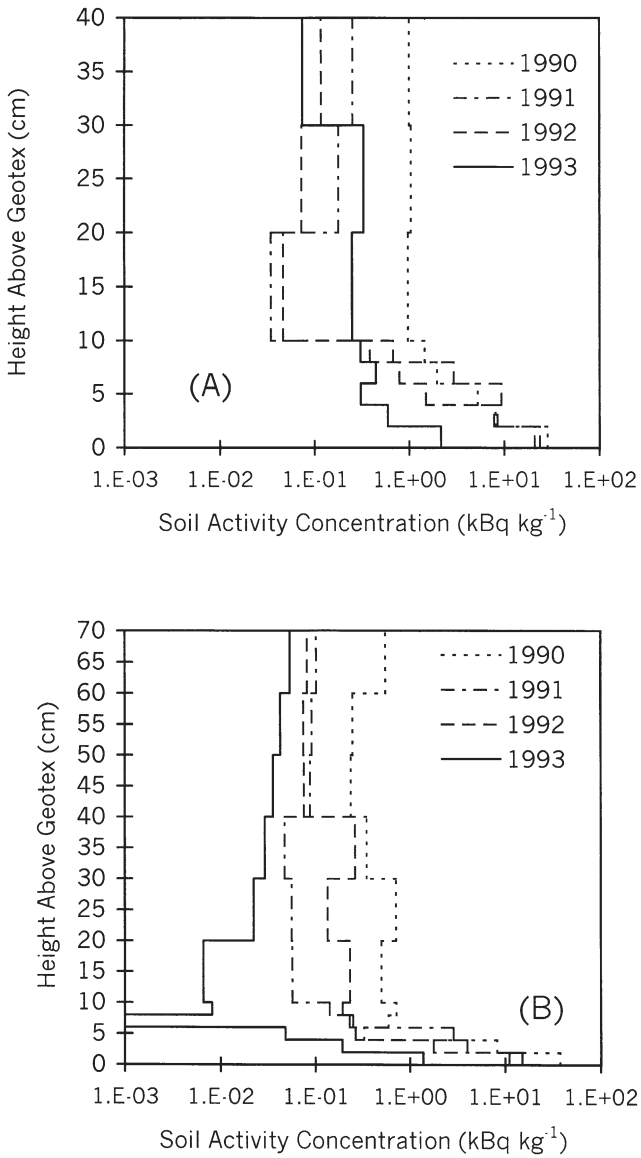

Fig. 2. Vertical distributions of ^{99}Tc activity concentrations in (A) shallow and (B) deep lysimeters from 1990 to 1993. The soil surface is located 40 and 70 cm above the geotextile material in the shallow and deep lysimeters, respectively.

where $[R]_i$ (Bq kg^{-1}) is the radionuclide activity concentration in the ith soil layer and f_i (dimensionless) is the fractional abundance of crop roots in the ith soil layer. This calculation allows each profile of activity concentrations shown in Fig. 1 and 2 to be reduced to a single average value. The WMAC values were used to compare the soil activity concentrations that are potentially accessible for crop root uptake from year to year and from lysimeter to lysimeter (Fig. 3, Table 3). For both radionuclides, WMAC decreased significantly between deep and shallow lysimeters. For ^{99}Tc, this difference was consistent from year to year; WMAC values for ^{99}Tc in shallow lysimeters were always greater than in deep lysimeters. The ^{99}Tc WMAC values decreased significantly from 1990 to 1993. The WMAC values for ^{36}Cl were significantly different between deep and shallow lysimeters and from year to year. The ^{36}Cl WMAC values were also consistently greater than those of ^{99}Tc by approximately one order of magnitude. Additionally, the significant interaction between both experimental factors (water table depth and year) for ^{36}Cl relates to the relative increase in ^{36}Cl WMAC in shallow lysimeters to deep lysimeters in 1992 and 1993 (Fig. 3A).

Table 2. Results of two-factor (fixed effects) ANOVA on vertical distributions of ^{36}Cl and ^{99}Tc activity concentrations (kBq kg^{-1}) in deep and shallow lysimeters from 1990 to 1993.

Radionuclide	Lysimeter	Year	Soil depth†	Year × soil depth interaction
^{36}Cl	shallow	***	***	***
	deep	***	***	***
^{99}Tc	shallow	***	***	NS‡
	deep	***	***	NS

*** Significant at the 0.001 probability level.
† Height above geotextile.
‡ Not significant at the 0.05 probability level.

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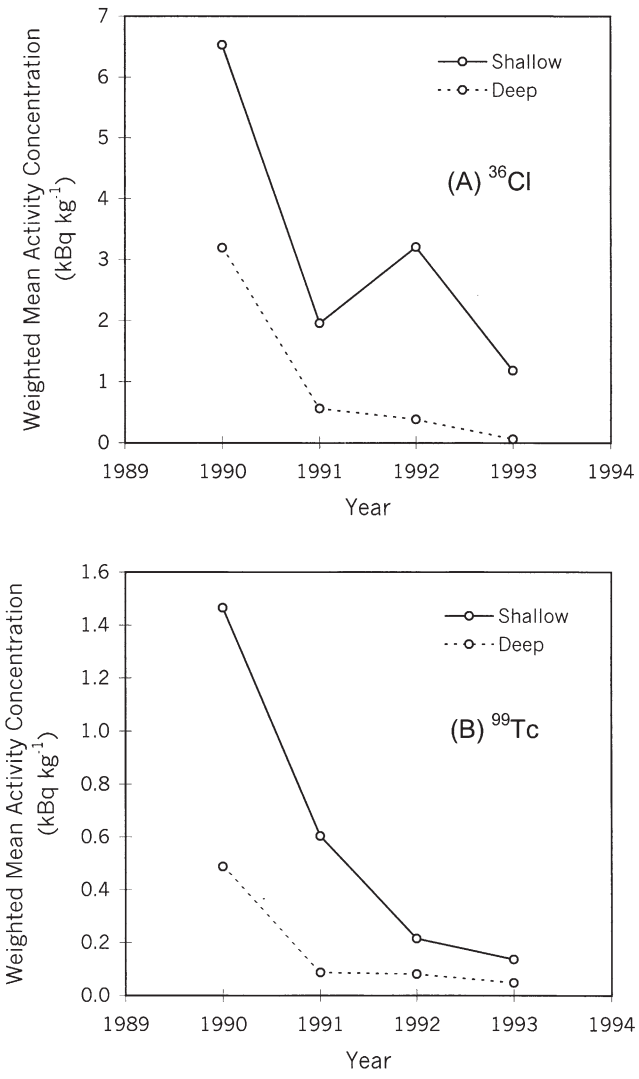

Fig. 3. Weighted mean activity concentrations of (A) ^{36}Cl and (B) ^{99}Tc in shallow and deep lysimeters from 1990 to 1993.

Soil-to-Plant Inventory Ratios

Total inventories of ^{99}Tc and ^{36}Cl (Bq) were calculated for the soil and the entire mass of wheat tissue removed at each harvest. Using these values, an inventory ratio was calculated to estimate the degree of gross transfer of each radionuclide from soil to crop. Gilbert and Simpson (1983) described this "inventory ratio" (IR) as:

$$\text{IR} = \frac{\text{plant activity per unit area soil (Bq m}^{-2})}{\text{soil activity per unit area soil (Bq m}^{-2})}$$

Table 3. Results of two-factor (fixed effects) ANOVA on weighted mean activity concentrations (WMAC) of ^{36}Cl and ^{99}Tc in deep and shallow lysimeters from 1990 to 1993.

Radionuclide	Year	Depth†	Year × depth interaction
^{36}Cl	***	***	***
^{99}Tc	***	**	NS‡

** Significant at the 0.01 probability level.
*** Significant at the 0.001 probability level.
† Depth of water table.
‡ Not significant at the 0.05 probability level.

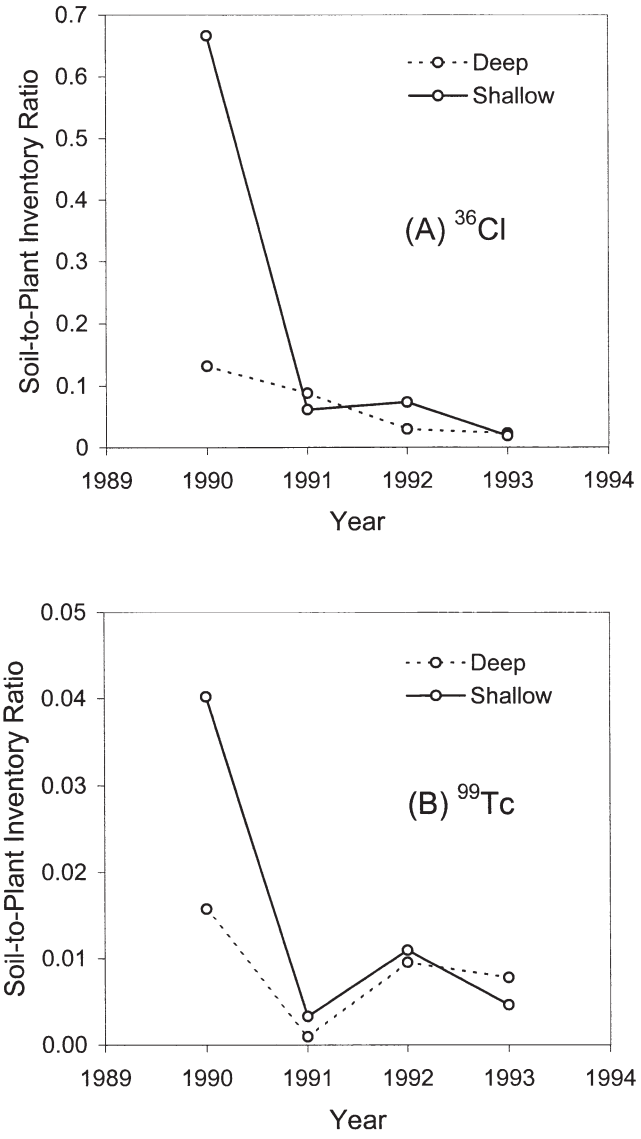

Fig. 4. Soil-to-plant inventory ratios of (A) ^{36}Cl and (B) ^{99}Tc in shallow and deep lysimeters from 1990 to 1993.

Inventory ratio values calculated for both ^{36}Cl and ^{99}Tc at harvest over the 4-yr experiment indicate that a significant fraction of the total lysimeter inventory was incorporated within crop tissues at harvest (Fig. 4). This was particularly true for ^{36}Cl, which at harvest in 1990 exhibited IR values of approximately 0.13 and 0.65 in deep and shallow lysimeters, respectively. The ^{36}Cl differences between deep and shallow lysimeters were highly significant, as was the decrease in IR value from 1990 to 1993 (Table 4). The IR values for ^{99}Tc were less than those for ^{36}Cl, though still relatively large at approximately 0.02 to 0.04 in 1990 for deep and shallow lysimeters, respectively. In contrast to ^{36}Cl, IR values for ^{99}Tc did not vary significantly either between deep and shallow lysimeters or from year to year (Table 4).

Weighted Soil-to-Plant Transfer Factors

Unlike the inventory ratio, the weighted soil-to-plant transfer factor (TF_w) can be used to estimate the overall

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Table 4. Results of two-factor (fixed effects) ANOVA on inventory ratios of ^{36}Cl and ^{99}Tc in deep and shallow lysimeters from 1990 to 1993.

Radionuclide	Year	Depth†	Year × depth interaction
^{36}Cl	***	**	**
^{99}Tc	NS‡	NS	NS

** Significant at the 0.01 probability level.
*** Significant at the 0.001 probability level.
† Depth of water table.
‡ Not significant at the 0.05 probability level.

efficiency of radionuclide uptake, which takes into account the relative distributions of radionuclide activity concentration and crop root density within the soil profile:

$$TF_w = \frac{[R]_{plant}\ (Bq\ kg^{-1})}{WMAC\ (Bq\ kg^{-1})}$$

where $[R]_{plant}$ is the activity concentration of a radionuclide within a specific plant tissue determined at harvest. Table 5 shows TF_w values for both ^{36}Cl and ^{99}Tc.

The TF_w values for ^{36}Cl varied significantly with year, water table depth, and tissue type. In shallow lysimeters, ^{36}Cl TF_w values for all wheat tissues decreased from 1990 to 1992 with a small increase in 1993. However, in deep lysimeters the pattern was more complex with a decrease in ^{36}Cl TF_w in 1991 followed by a dramatic increase in 1992 and 1993. The TF_w values for ^{99}Tc varied significantly with water table depth and tissue type, though not from year to year. In general, TF_w values for ^{99}Tc were significantly greater in deep lysimeters and lower in shallow lysimeters, with the exception of 1993 in which TF_w values were higher in shallow lysimeters. Wheat grain, in general, had significantly lower TF_w values for ^{99}Tc than did leaf, chaff, and stem tissues.

The TF_w values for ^{36}Cl and ^{99}Tc were significantly different with ^{36}Cl exhibiting a much greater absolute soil-to-plant transfer and year-to-year variability in soil-to-plant transfer than ^{99}Tc. For deep and shallow lysimeters in 1990, the ^{36}Cl TF_w value for stem tissue was approximately eight to nine times greater than that for ^{99}Tc. The effect of water table depth on crop uptake was also different for both radionuclides. Whereas ^{36}Cl TF_w values were substantially greater for shallow lysimeters than for deep lysimeters in 1991, this trend was reversed in 1993, leading to a significant interaction between the year of the experiment and water table depth. This trend was also observed for soil activity concentration profiles of ^{36}Cl (Table 2). Differences in TF_w values of ^{99}Tc between deep and shallow lysimeters were more consistent, with TF_w values for deep lysimeters exceeding those from shallow lysimeters in 11 out of 16 cases (four tissues types over 4 yr give 16 data pairs [deep vs. shallow] for comparison). The differences between TF_w values for ^{99}Tc in deep and shallow lysimeters were significant, though the interaction between water table depth and year was not significant (Table 6). This suggests that, in general, soil-to-plant transfer of ^{99}Tc was more efficient in deep lysimeters in which a greater depth of soil was present in the oxic state. There was a significant interaction between the year of harvest and the tissue type for the TF_w for ^{99}Tc, demonstrating that the distribution of ^{99}Tc between different tissues of the crop varied from year to year.

DISCUSSION

The results obtained for both ^{36}Cl and ^{99}Tc confirm the hypothesis that these radionuclides exhibit high levels of geochemical mobility and biological incorporation. Previous information on ^{99}Tc suggested it to be the most highly mobile and biologically available radionuclide, with observed ranges of soil-to-plant TF values commonly exceeding unity (International Union of Radioecology, 1989). Experimental studies have shown that, in common with its likely nutrient analogue NO_3^-, $^{99}TcO_4^-$ is incorporated to such a degree by crops that significant depletion of ^{99}Tc within the soil can be observed after a single growing season (Grogan, 1984). The soil-to-plant inventory ratios observed in this study suggest that harvest of the wheat crop resulted in the removal of approximately 2% of the total ^{99}Tc inventory within the soil.

Until now, data on the ability of crops to remove ^{36}Cl from contaminated soils have been absent. The inventory ratios calculated for ^{36}Cl in this study confirm the speculative statement (Coughtrey et al., 1983) that radiochlorine in soils was likely to be depleted by crop uptake. At harvest in 1990, IR values of 0.65 and 0.13 indicate that approximately 40 and 12% of the total ^{36}Cl inventory in the shallow and deep lysimeters, respectively, was located within the winter wheat crop in this experiment, although this percentage decreased dramatically in subsequent years. The soil-to-plant transfer of ^{36}Cl represented by these IR values was extremely high, even when compared with previously obtained soil-to-plant transfer factors for ^{99}Tc. Thus, even though the intrinsic radiotoxicity of ^{36}Cl is low (International Atomic Energy Agency, 1996) its high mobility in the geosphere and its very high soil-to-plant transfer factor have the potential to make it a priority radionuclide in the context of solid radioactive waste disposal (Sheppard et al., 1996; Nirex, 1997). Sheppard et al. (1996) identified the soil-to-plant transfer pathway as particularly significant for ^{36}Cl derived from radioactive waste disposal facilities; the data presented in this paper support this conclusion.

An effect noted in previous work on radioisotopes of Cs, Co, and Na (Wadey et al., 1994, 2001) was an apparently greater root uptake efficiency, as measured by higher weighted soil-to-plant transfer factors, from lysimeters with deep water tables. This is thought to be due to the creation of physicochemical conditions within the anoxic region of the water table and capillary fringe, which can enhance the bioavailability of cationic radionuclides such as conversion of nitrogen to the NH_4^+ form, which can then de-sorb cations from soil exchange sites. With ^{36}Cl, however, the differences in TF_w between deep and shallow lysimeters were not so clear, since we measured a larger uptake from shallow lysimeters in 1991 and, later (1993) measured greater uptake from deep lysimeters. This reversal in the relative ^{36}Cl uptake from deep and shallow lysimeters was brought about mainly by the high degree of year-to-year variability in

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Table 5. Weighted soil-to-plant transfer factors (dimensionless; values are means with standard deviations) for wheat growing in deep and shallow lysimeters from 1990 to 1993.

		^{36}Cl				^{99}Tc			
		Shallow		Deep		Shallow		Deep	
Year	Plant part	Mean	SD	Mean	SD	Mean	SD	Mean	SD
1990	grain	192.8	83.14	126.2	77.9	0.649	0.836	13.87	14.75
	chaff	361.7	110.5	204.7	132.8	45.98	42.87	151.5	122.5
	leaf	851.7	421.8	529.3	267.1	183.4	151.6	411.8	396.0
	stem	1449	509.3	953.5	588.2	159.4	153.5	112.6	44.40
1991	grain	42.14	15.39	0.089	0.071	6.467	7.579	9.689	16.60
	chaff	80.22	55.74	0.122	0.074	4.992	4.385	10.88	11.96
	leaf	105.0	58.02	0.218	0.117	44.12	68.20	49.91	63.46
	stem	276.8	148.8	0.055	0.061	16.27	11.08	20.59	15.29
1992	grain	19.40	6.655	21.27	31.86	12.22	20.90	16.46	13.24
	chaff	44.47	61.17	11.36	13.44	37.00	66.29	140.9	233.3
	leaf	29.60	15.56	11.48	10.53	85.54	141.7	136.2	170.9
	stem	192.5	73.72	400.5	444.1	44.20	35.53	1001	1853
1993	grain	42.22	31.15	886.9	1121	57.47	92.65	27.19	37.06
	chaff	86.07	49.03	2651	4350	53.50	47.54	45.14	32.47
	leaf	60.45	26.05	2790	4835	132.4	141.7	53.41	27.24
	stem	302.0	143.8	6425	7995	87.11	135.4	44.00	66.20

^{36}Cl uptake from deep lysimeters. For ^{99}Tc, larger TF_w values (11 out of 16 cases, $p < 0.01$) were generally evident in deep lysimeters than in shallow lysimeters, though the differences in IR values between deep and shallow lysimeters were not significant. More efficient uptake of ^{99}Tc from the deep lysimeters can be explained by the fact that a larger depth of soil above a deep water table would be expected to give rise to oxic conditions in which the biologically available TcO_4^- ion was predominant over reduced forms of ^{99}Tc.

Increased uptake of radionuclides from shallow lysimeters might be expected for $^{36}Cl^-$ as the relative density of plant roots within the water table is greater in shallow than in deep lysimeters (Wadey et al., 2001). It appears that for cationic radionuclides, the reduced density of roots in the region of deeper and more anoxic water tables is offset by enhancement of radionuclide bioavailability. Since ^{36}Cl is anionic, however, the production of NH_4^+ ions at low redox potentials is not likely to exert any effect on its physicochemical sorption or on its bioavailability. A direct conversion from $^{99}TcO_4^-$ (Tc^{VII}) to the more highly sorbed $^{99}TcO_2$ (Tc^{IV}) would be expected at the low redox potentials in the region of the water table. According to data presented by Beasley and Lorz (1986), within a pH range of 6 to 8 (the pH range of the soil used in the lysimeter experiment) the conversion of Tc^{VII} to Tc^{IV} takes place at a redox potential of approximately 150 mV. Redox potentials in both deep and shallow lysimeters frequently fell below 150 mV during the last two years of the experiment. Figure 5 indicates that conditions for reduction of $^{99}Tc^{VII}$ to its less mobile and less available form persisted more than 90% of the time at soil depths within 5 to 10 cm of the water table in deep lysimeters, and with a lower frequency (75–80%) within a similar distance in the shallow lysimeters. It is also clear from this figure that in the regions 10 cm above deep and shallow water tables, the dominant form of ^{99}Tc is likely to have been $^{99}TcO_4^-$ in both deep and shallow lysimeters. This is also the region where wheat roots are abundant and ^{99}Tc is readily absorbed by plants. This indicates that ^{99}Tc must have migrated across the redox "barrier" in the region of the water table. The net balance of these processes is that overall root uptake efficiency, as measured by TF_w values, is significantly greater for deep lysimeters.

The ^{36}Cl uptake by winter wheat in this study showed a systematic and significant decrease each year from 1990 to 1993. This trend indicates a decreased overall efficiency of crop uptake with time. The pattern was more complex in the case of the TF_w for ^{36}Cl in the deep lysimeters, although interpretation of TF_w is complicated by the year-on-year variation in the pattern of root density distributions reported in the previous paper in this series (Wadey et al., 2001). The data show that TF_w values for ^{36}Cl in shallow lysimeters only decreased significantly from 1990 to 1991 and showed no further decreases thereafter: TF_w values for ^{36}Cl in deep lysimeters decreased significantly from 1990 to 1991 then increased significantly from 1992 to 1993, possibly in response to precipitation and water balance. Wadey et al. (2001) summarized the rainfall inputs and water balances within the lysimeter system from 1990 to 1993. During the first spring and summer of the experiment, 1990, rainfall was only 40% of the average in the four

Table 6. Results of three-factor (fixed effects) ANOVA on data describing the weighted soil-to-plant transfer factors (TF_w) of ^{36}Cl and ^{99}Tc in deep and shallow lysimeters from 1990 to 1993.

	Factor			Interaction			
Radionuclide	Year	Depth†	Tissue	Year × depth	Year × tissue	Depth × tissue	Year × depth × tissue
^{36}Cl	***	***	***	***	NS‡	NS	NS
^{99}Tc	NS	**	***	NS	**	NS	NS

** Significant at the 0.01 probability level.
*** Significant at the 0.001 probability level.
† Depth of water table.
‡ Not significant at the 0.05 probability level.

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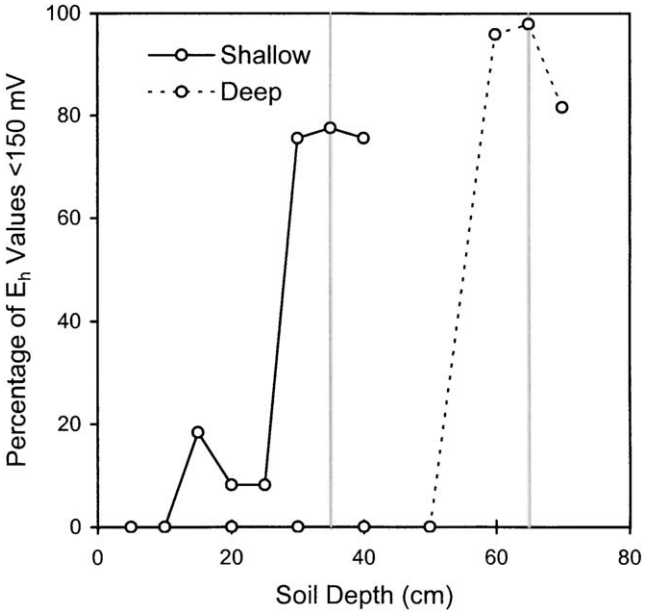

Fig. 5. Plots of the percentage of soil redox (E_h) measurements (49 measurements made fortnightly between August 1992 and July 1994) to fall below 150 mV, the approximate redox potential at which Tc^{VII} is likely to be reduced to Tc^{IV} at soil pH values of between 6 and 8. The vertical lines represent water table depths in shallow and deep lysimeters (35 and 65 cm, respectively).

spring and summer seasons of the experiment. The low rainfall resulted in substantial net water fluxes up the soil profile from the fixed water tables. Net water fluxes in all subsequent years were downward through the soil profiles. This might have resulted in the dramatic ^{36}Cl uptake by the crop in 1990, followed by decreasing or stationary uptakes, depending on which measure of crop uptake (IR or TF_w) was adopted, in 1991 to 1993. The strong net upward water fluxes in 1990 were particularly exaggerated in the shallow lysimeters, and the pronounced decline in ^{36}Cl IR from 1990 to 1993 for shallow lysimeters, in particular (Fig. 4A), lends weight to the argument that water fluxes are of key importance in controlling the migration and subsequent plant uptake of poorly sorbed radionuclides in soils.

Another possible explanation for the decline in ^{36}Cl IR values within the lysimeters is that ^{36}Cl became either less accessible or less bioavailable with time. The issue of accessibility of radionuclides to roots in soils was addressed by Wadey et al. (1994) and relates to the relative vertical distributions of radionuclide activity concentrations and roots within the soil profile. For example, if a radionuclide is absent from the root zone, then it can be considered inaccessible or unavailable. The use of the WMAC and TF_w in this study attempts to correct for different degrees of radionuclide accessibility between lysimeters and between years. The fact that WMAC values for deep and shallow lysimeters decreased significantly during the experiment (Fig. 3) suggests that declining IR values and, from 1990 to 1991, decreasing TF_w values can be explained by changes in the relative vertical distributions of ^{36}Cl and crop roots. On the other hand, if this decrease were to be ascribed to a time-dependent loss of bioavailability of ^{36}Cl then some form of chemical interaction of radiochlorine with the soil solid phase would have to be identified. The presence of ^{36}Cl in the Cl^- form would not facilitate this kind of interaction, although we have previously presented evidence to suggest that such an interaction occurs (Lee et al., 2001). It appears that specific association between ^{36}Cl and low molecular weight components of the soil's humic substances can occur, thus reducing the chemical extractability of ^{36}Cl from the soil and, presumably, its bioavailability. In a recent lysimeter experiment Rodstedth et al. (2003) reported "storage" in lysimeter soils of chlorine in an organic form, which led to discrepancies between inputs and outputs of chlorine in the system, possibly a confirmation of our results.

Other controls on ^{36}Cl and ^{99}Tc behavior in the soil–plant system are possible but have not been studied in detail as part of the experiment reported here. In particular, stable Cl^- can influence the migration and uptake of ^{36}Cl, and Cl^- concentrations in soils can vary substantially due to factors such as inputs of marine aerosols (Farrell et al., 1993). In the case of ^{99}Tc, it has already been mentioned that the nitrate anion (NO_3^-) is known to be an analogue of the most bioavailable form of ^{99}Tc, $^{99}TcO_4^-$. Thus, increasing concentrations of nitrate in the soil have the effect of reducing $^{99}TcO_4^-$ absorption by plants (Van Loon, 1986; Echevarria et al., 1998). Nitrate may provide an important seasonal and climatic control on $^{99}TcO_4^-$ uptake by plants since NO_3^- levels in soils can vary substantially in the temperate regions at different times of the year and from one climatic region to another. Such considerations have potentially important implications for safety assessments of radioactive waste repositories over thousands of years, but were outside the scope of the lysimeter study reported here.

It is difficult to compare the absolute TF_w values calculated for both ^{36}Cl and ^{99}Tc in this study with more conventionally calculated TF values, which do not account for the vertical distributions of radionuclides or plant roots in the soil profile. However, the comparison between TF_w values in this study for ^{36}Cl and ^{99}Tc can be used to gauge the likely magnitude of ^{36}Cl uptake by crops relative to other radionuclides. Many other studies have suggested that soil-to-plant transfer factors for ^{99}Tc are at the upper end of the TF range when compared with all other environmentally significant radionuclides, even when subject to constraints on its mobility due to low redox potentials (Sheppard and Evenden, 1985). On the basis of the results presented here, the hitherto poorly investigated ^{36}Cl seems likely to exceed even ^{99}Tc in its potential to contaminate vegetation and is therefore clearly a radionuclide worthy of considerable attention, not necessarily only in the context of solid radioactive waste disposal.

CONCLUSIONS

In this study we have demonstrated that ^{99}Tc and ^{36}Cl are taken up by wheat from soils initially contaminated below the surface. Uptake of ^{36}Cl by winter wheat in this study was sufficient to deplete the total measured

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inventory in lysimeter soils by up to 40% in one cropping season. This is due to the presence of ^{36}Cl within the soil as a highly mobile and bioavailable anion $^{36}Cl^-$. The chemical speciation of ^{99}Tc in soils in this experiment is likely to have been strongly controlled by changes in redox potentials within and above the lysimeter water tables, with the highly mobile and bioavailable TcO_4^- (Tc^{VII}) predominating in the aerobic, unsaturated regions and the more highly sorbed $^{99}TcO_2$ (Tc^{IV}) predominant in the saturated regions. Aside from chemical speciation, major controls on the migration and plant uptake of both ^{99}Tc and ^{36}Cl are likely to include water flux, which is itself controlled by climatic conditions, and the presence of stable Cl^- in the case of ^{36}Cl and NO_3^- in the case of ^{99}Tc.

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