Soil availability, plant uptake and soil to plant transfer of ^{99}Tc—A review

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Abstract

The fission yield of ^{99}Tc from ^{239}Pu and ^{235}U is similar to that of ^{137}Cs or ^{90}Sr and it is therefore an important component of nuclear weapons fall-out, nuclear waste and releases from nuclear facilities. There is particular current interest in ^{99}Tc transfer from soil to plants for: (a) environmental impact assessments for terrestrial nuclear waste repositories, and (b) assessments of the potential for phytoextraction of radionuclides from contaminated effluent and soil. Vascular plants have a high ^{99}Tc uptake capacity, a strong tendency to transport it to shoot material and accumulate it in vegetative rather than reproductive structures. The mechanisms that control ^{99}Tc entry to plants have not been identified and there has been little discussion of the potential for phytoextraction of ^{99}Tc contaminated effluents or soil. Here we review soil availability, plant uptake mechanisms and soil to plant transfer of ^{99}Tc in the light of recent advances in soil science, plant molecular biology and phytoextraction technologies. We conclude that ^{99}Tc might not be highly available in the long term from up to 50% of soils worldwide, and that no single mechanism that might be easily targeted by recombinant DNA technologies controls ^{99}Tc uptake by plants. Overall, we suggest that Tc might be less available in terrestrial ecosystems than is often assumed but that nevertheless the potential of phytoextraction as a decontamination strategy is probably greater for ^{99}Tc than for any other nuclide of radioecological interest.
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Contents

1. Introduction

Extensive reviews in 1984 (Desmet and Mytteneare, 1984) and 1989 (Wildung et al., 1989) confirmed the usefulness of understanding the movement of ^{99}Tc in the environment. Since then, advances in soil science and molecular biology have provided new information with which to assess its behaviour in terrestrial environments. Interest in predictions of soil to plant transfer of ^{99}Tc is increasing because of their importance to environmental impact assessments for permanent terrestrial nuclear waste repositories (Ecchevaria et al., 1998). Discharges of ^{99}Tc to the marine environment have received much attention in recent years (Brown et al., 1999) providing added incentive to dispose of ^{99}Tc in permanent terrestrial repositories. In addition, as part of decontamination and decommissioning assessments, there is current interest in the potential of plants to extract toxic elemental pollutants, including radionuclides such as ^{99}Tc, from contaminated effluents and soils (Meagher, 2000; Willey et al., 2002).

2. The availability of ^{99}Tc in soils

2.1. The speciation of ^{99}Tc

The electron configuration of Tc is $[Kr]4d^65s^1$, so few if any cations are predicted, although metal–metal bonds are possible (Pourbaix, 1966; Mousny et al., 1979; Rosetti, 1998). The Tc configuration is similar to that of molybdenum ($[Kr]4d^55s^1$) and manganese ($[Ar]3d^54s^2$) but with a shift in favour of higher oxidation states. Tc can exist in all valence states from +7 to −1 but the +7, +4 and 0 states are the most stable (Curtis et al., 1999; Rosetti, 1998). TcO_4^- is produced during the processing of nuclear fuel, and is the ion most likely to be released into the environment (Till, 1984; Harms et al., 1999a). The pE–pH stability diagram for Tc predicts that TcO_4^- will be stable in aerobic soils and that reduced species can be formed in anaerobic soils (Leiser and Bauscher, 1987).

2.2. ^{99}Tc in aerobic and anaerobic soils

TcO_4^- does not sorb onto negatively charged "cation" exchange sites and is thus generally reported to be available to pedological and biological processes in aerobic sediments and soils (Zeevaert et al., 1989; Echevarria et al., 1997). Sheppard et al., (1990) found no indication of sorption for a large number of Canadian soil types, whatever the organic matter content. Takahashi et al., (1999) and Van Loon et al., (1984) showed that TcO_4^- is not complexed with humic acid, but remains free in the soil solution under aerobic conditions. Complexation of TcO_4^- with humic acid and other dissolved organic carbon is only possible when the *Eh*-value becomes negative ($E_0 = -0.50$ V for Tc(VII)/Tc(IV)), (Rößler et al., 2000). As noted by Lieser and Bauscher (1987), this is principally possible under anaerobic conditions in the presence of pyrite containing rocks via Fe^{2+} ($E_0 = -0.77$ V). Conditions in which humic acids might be important for the mobility of ^{99}Tc are therefore infrequent in soils. Aerobic soil microflora are unable to reduce or accumulate TcO_4^- (Henrot, 1989). Literature reports therefore suggest that neither chemical nor biological factors have much impact on the generally high availability of ^{99}Tc in aerobic soils.

In anaerobic soils, especially those high in organic matter, the movement of ^{99}Tc is strongly retarded, probably as TcO_2 (Sheppard et al., 1990; Tagami and Uchida, 1996; Tagami and Uchida, 1997). It is much less available to plants from anaerobic than from aerobic soils (Sheppard et al., 1990; Yanagisawa and Muramatsu, 1995; Tagami and Uchida, 1996). TcO_2 can be sorbed to the soil solid phase in reducing conditions by complexation with organic matter, and sorption is enhanced at high clay contents and high pH (Sheppard et al., 1990; Rößler et al., 2000). TcO_2 complexes are re-oxidised very slowly, limiting the release of TcO_4^- into the soil solution (Sheppard and Evenden, 1991; Echevarria et al., 1997). For example, Tagami and Uchida (1999) noted that a dry aerobic period after waterlogging did not remobilise TcO_2. Sheppard and Evenden (1991) showed that aquatic macrophytes known for their ability to oxidise their rhizosphere, such as rice, are unable to oxidise ^{99}Tc in flooded anaerobic soils sufficiently quickly to enhance its availability. Oxidation of

^{99}Tc compounds is probably so slow that accumulation of ^{99}Tc is possible in soils that are subjected to periodic waterlogging (Yanagisawa and Muramatsu, 1993, 1995; Tagami and Uchida, 1999). However, there are a number of reports of ^{99}Tc being remobilised from marine sediments (Masson et al., 1989; Leonard et al., 1997; Morris et al., 2000). Low redox potentials can also cause TcO_4^- to react with hydrogen sulphide to form Tc_2S_7 which is not available to plants (Brookins, 1988; Tagami and Uchida, 1996; Tagami and Uchida, 1997). Lloyd et al. (2000) showed that Fe(III) reducing bacteria may be responsible for the reduction of Tc(VII) in sediments and it seems likely that related bacteria carry out a similar process in anaerobic soils. Overall, although a much smaller range of soils has been investigated than for ^{137}Cs, for example, reports in the literature suggest that ^{99}Tc is likely to be highly available in aerobic soils and unavailable in anaerobic soils. However, it is worth considering the chemistry of ^{99}Tc in a wider range of soils than have thus far been investigated experimentally.

2.3. ^{99}Tc and soils of the world

It has been reported that ^{99}Tc availability is generally higher for sandy soils than for clay soils (Bell et al., 1988), indicating that surface area, and hence adsorption, has some role in determining availability. In many aerobic soils there is anion exchange capacity that derives from the pH dependent charge on sesquioxides and organics. There has been much recent study of the adsorption of SO_4^{2-} (Karltun, 1997) and HPO_4^{2-} (Geelhoed et al., 1997) at anion exchange sites and it is now of established pedological importance for a range of anions (Bellini et al., 1996; Barreal et al., 2001). In many aerobic temperate soils anion exchange is low but oxisols, for example, have high concentrations of sesquioxides, are acidic, and have a high anion exchange capacity due to pH dependent charges on the sesquioxides (USDA, 1999). Oxisols cover nearly 15% of the planet's surface and are located primarily in South America and sub-Saharan Africa. Their TcO_4^- adsorption properties have seldom been investigated and may be substantial. The contribution of pH-dependent anion exchange capacity to Tc adsorption is, therefore, not yet fully known. It seems likely to be less important than for HPO_4^{2-} or SO_4^{2-} because the lyotropic series in general is $HPO_4^{2-} > SO_4^{2-} \gg Cl^-/NO_3^-$ but might be significant in at least one important soil type. Increased adsorption of ^{99}Tc reported with increasing organic matter and decreasing pH (Cataldo et al., 1983) is consistent with pH-dependent anion exchange sites on organic matter.

There are also important soil types that have a permanent and predominant anion exchange capacity. The work of the International Committee on the Classification of Andisols has arisen from andisols being classified as one of the 12 soils orders in the USDA system of soil taxonomy (USDA, 1999). Andisols cover 125 million hectares, i.e. approximately 1% of the land surface. Andisols are derived from volcanic ejecta and contain high concentrations of allophane and other poorly crystalline materials. They have a very high adsorption capacity for $H_2PO_4^-$ and other anions including Cl^- and NO_3^- (Katou et al., 1996, Shamshuddin et al., 1996). Allophane is known to have a high ^{99}Tc adsorption capacity and has been investigated for

limiting ^{99}Tc spread from waste repositories. The data of Yanagisawa and Muramatsu (1995) show that andisols produce relatively low transfer to plants, presumably because of relatively high adsorption in the soil. Further, there are a range of non-volcanic soils with andic properties and a high anion exchange capacity (Barreal et al., 2001).

The obvious importance of anaerobic soils to rice production should not detract from the wider ecological importance of anaerobicity in soils. About 6% of the land surface area is covered with wetlands in which the soil is permanently waterlogged (Armstrong et al., 1994). In addition, histosols and spodosols are both frequently waterlogged, especially at high latitudes and altitudes. Histosols are primarily organic and spodosols have deep organic surface horizons that often form a rooting zone with high adsorption of ^{99}Tc. These soil orders cover a large proportion of land area at high latitudes and approaching 10% of the total land surface (USDA, 1999). Further, in much of the temperate zone and the wet tropics, soils are waterlogged periodically. This might help to explain why both laboratory (Mousny and Myttenaere, 1981; Tagami and Uchida, 1998) and field studies (Hoffman et al., 1982; Garten et al., 1984) have found that, even in aerobic soils, the proportion of available ^{99}Tc is reduced over time. Anaerobic microsites in aerobic soils, often produced within soil aggregates as the water-filled pore space increases, are now recognised to be important in denitrification and the production of ammonium on a global scale (Davidson et al., 2000). It seems likely that they might also play a role in progressive immobilization of ^{99}Tc. A number of authors have previously suggested that anaerobic microsites in soils might be important in TcO_4^- reduction (Hoffman et al., 1982; Henrot, 1989; Echevaria et al., 1997) but the potential scale of the process may only now be emerging with recent research into denitrification.

3. Mechanisms of ^{99}Tc uptake by plants

3.1. Ion uptake mechanisms in plants

The movement of TcO_4^- from the soil solution into plant tissue is very often the first step in the entry of ^{99}Tc into terrestrial foodchains. When adsorption to the soil is low, as is often the case for ^{99}Tc, plant uptake controls plant concentrations (Van Loon et al., 1989). The mechanisms that control plant uptake can therefore determine foodchain contamination. There has been some debate, as yet unresolved, about the mechanisms through which TcO_4^- enters plants. Plants take up TcO_4^- rapidly with kinetics characteristic of nutrient uptake. For example, Wildung et al., (1977) and Cataldo et al. (1983) suggested that multiphasic uptake, including dependence on metabolic energy, indicated entry through saturable, active transport mechanisms that conformed to Michaelis–Menten kinetics. The mathematical model of ^{99}Tc uptake developed by Van Loon et al. (1989) is also consistent with uptake as a nutrient analogue.

Root plasma membranes generally have an inside negative electrical potential difference of about -150 mV generated by a P-type H$^+$-ATPase, which pumps out H$^+$

ions. At most concentrations found in soil solution and root cells, the membrane potential tends to drive passive cation uptake. In contrast, accumulation of anions such as TcO_4^- is strongly against the electrochemical gradient and requires active transport. Thus, plants are generally able to exclude non-nutrient anions from uptake if they are dissimilar in size and charge from nutrient ions. In the past decade, knowledge of transport systems of plants has been transformed and the proteins involved in the uptake of a variety of nutrients identified (e.g. Crawford and Glass, 1998). This has culminated in estimates from genome studies of how many genes and proteins are associated with ion transport processes. In *Arabidopsis thaliana* approximately 13.1% of the genome encodes transporters, i.e. about 2,300 proteins (Arabidopsis Genome Initiative, 2000). Of these about 21% are ATP dependent transporters likely to be involved in active transport (Arabidopsis Genome Initiative, 2000), although not all will be located in the root plasma membrane. As a result of such research it is now possible to assess at the molecular level the mechanisms associated with plant uptake of a contaminant such as [99]Tc.

3.2. Tc uptake and sulphate transport

Molecular studies have now isolated 20 sulphate transporters from a variety of plants (Hawkesford, 2000), including seven from *Arabidopsis thaliana* (Saito, 2000). There are great similarities in SO_4^{2-} transporters from all eukaryotes but, in general, plant sulphate transporters fall into distinct subgroups with one group of three specialised for root uptake (Hawkesford, 2000). Plants seem likely to have two root sulphate transporters of high affinity and one of lower affinity (Fig. 1). These proteins have similar amino acid sequences and, from homology with other transporters, are thought to be H^+/SO_4^{2-} co-transporters. Their structure/function relationships are not yet clear (Smith et al., 2000) but it seems likely that amino acid residues on hydrophilic loops between the membrane spanning domains influence specificity. In particular, the influence of the arginine antagonist hydroxyphenylgloxal on SO_4^{2-} transport indicates that exposed arginine residues on hydrophilic loops may be involved in SO_4^{2-} binding (Clarkson et al., 1992). At physiological pH, the TcO_4^- anion will probably be able to bind to these sites, which are likely to be on the positively charged guanidino side chain of arginine. This means that TcO_4^- can probably be transported to some extent by this protein. However, it is unlikely to be able to compete effectively for binding sites on the arginine with SO_4^{2-}, especially at the concentrations of the two ions likely in the soil solution. It seems likely that SO_4^{2-} binding is similar to that in sulphate reducing bacteria in which monovalent anions can bind to, but cannot compete effectively for, binding sites (Postgate, 1984). This would explain the depression of TcO_4^- uptake by SO_4^{2-}. It is, however, difficult to envisage the reported levels of ^{99}Tc getting into plants entirely though these transport proteins from solutions or soils that contain high enough sulphate concentrations to enable plants to grow.
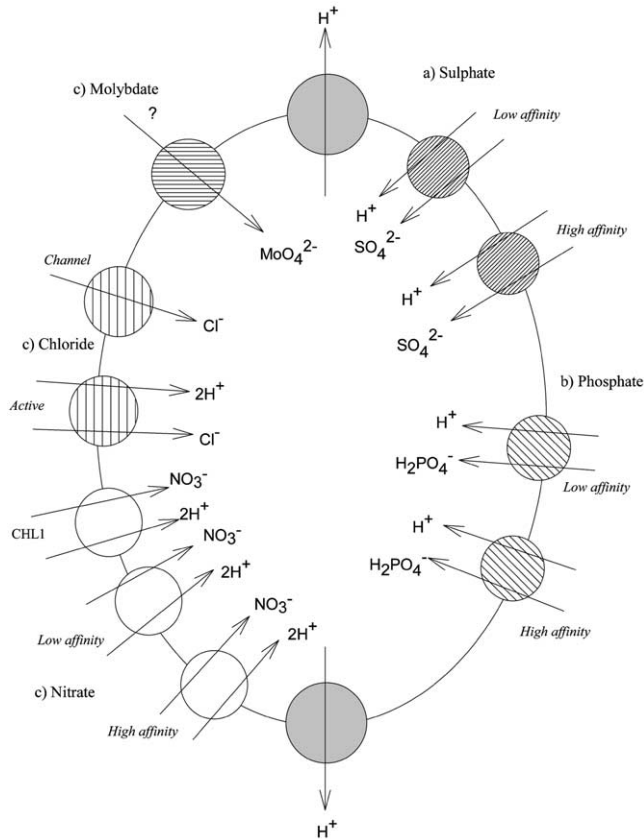
Fig. 1.   Types of plant root cell transport protein potentially involved in ^{99}Tc uptake by plants.

3.3. Tc uptake and phosphate transport

Plants contain a suite of transport proteins for phosphate. They are $H^+/H_2PO_4^-$ co-transporters, a type of transporter known only from fungi and plants (Raghothama, 2000). As with sulphate, there are sub-groups of plant phosphate transporters including those expressed in roots (Smith et al., 2000) (Fig. 1). In *Arabidopsis* nine genes encoding for high affinity phosphate transporters have been reported and they have very high sequence homology with transporters in a range of other plant species, suggesting that these are amongst the oldest and most highly conserved of plant proteins (Raghothama, 2000). Soil pH and the pK_a for inorganic phosphate indicate that $H_2PO_4^-$ is the phosphate species most likely to be transported across the plasma membrane but little is known about mechanisms of specificity (Raghothama, 2000). It is likely, however, that the long loop of hydrophilic amino acids between the two groups of six membrane spanning domains will affect specificity. The soil concentration of $H_2PO_4^-$ is often much lower than that of SO_4^{2-}, and TcO_4^- is likely to be

able compete more effectively against the univalent $H_2PO_4^-$ for binding sites on transporters than against the divalent SO_4^{2-}. We suggest that it would be interesting to use molecular techniques to dissect the importance of $H^+/H_2PO_4^-$ transporters in plant uptake of TcO_4^- because it seems likely to have been underestimated. Suzuki et al. (2000) showed that mycorrhizal plants can have higher ^{99}Tc uptake rates than non-mycorrhizal plants, which is consistent with uptake through $H_2PO_4^-$ pathways.

3.4. Tc uptake and nitrate transport

In 1998, Echevarria et al. reported that NO_3^- additions can suppress TcO_4^- uptake in pot-grown *Lolium perenne*. A number of nitrate transport proteins have now been isolated from plants (Crawford and Glass, 1998; Forde and Clarkson, 1999) (Fig. 1). A sub-group is expressed in plant roots (Liu et al., 1999). They are $2H^+/NO_3^-$ co-transporters. It seems likely that TcO_4^- can be transported by them, but how fast this can occur in the presence if nitrate will be interesting to ascertain. Some high affinity NO_3^- transport proteins react very rapidly to external NO_3^- concentrations, being expressed primarily in the presence of external nitrate, and can rapidly be switched off when plants are fed with NH_4^+ (Crawford and Glass, 1998). This may help to explain the absence of competition effects noted in plants that have not been exposed to nitrate for 24 h or more and fed with NH_4TcO_4 (e.g. Cataldo et al., 1983). However, we suggest that as NO_3^- transporters are expressed at high levels in many plant roots a proportion of ^{99}Tc might enter plants through them. Interestingly, in anaerobic soils where NO_3^- is absent plants do not express important high affinity NO_3^- transport proteins (Forde and Clarkson, 1999). This might contribute to the lower uptake of TcO_4^- reported from anaerobic soils.

3.5. Tc uptake and the transport of other ions

If TcO_4^- is an analogue of a macronutrient, then it would be reasonable to expect root and shoot concentrations to exceed those measured by, for example, Echevarria et al. (1998). In fact, numerous studies have shown that, regardless of the Tc concentration in the soil, there is a maximum concentration of about 0.1 mg kg^{-1} plant (Lembrechts and Desmet, 1985; Masson et al., 1989; Echevarria et al., 1997; Krijger et al., 1999). Bell et al. (1988) reported that Tc levels in *Pisum sativa* did not exceed 0.07 ppm. Echevarria et al. (1998) found that the maximum activity concentration measured within *L. perenne* leaves did not exceed 0.03 mg Tc kg^{-1} plant biomass from an initial concentration of 0.05 mg Tc kg^{-1} (29.6 kBq). These concentrations are much lower than expected of an analogue of the macronutrient ions sulphate, phosphate or nitrate.

Cl^- is the micronutrient plants require in the greatest amount. There are active Cl^- transporters that move Cl^- through the root plasmamembrane (White and Broadley, 2001). They are an important class of anion transporter whose role in ^{99}Tc transport is uninvestigated. Few competition effects between Cl^- and TcO_4^- have been reported but as charge is an important criterion in selectivity it is possible that active Cl^- transporters also have a role in TcO_4^- uptake. However, the chemical

properties of technetium are most similar to the micronutrients manganese and molybdenum (Mousny et al., 1979). Manganese is transported into plants in the cationic form (Mn^{2+}) and is relatively immobile within plants (Marschner, 1995). Molybdenum is absorbed as molybdate (MoO_4^{2-}). As an essential micronutrient it is likely that molybdate transport proteins exist in plant roots (Fig. 1), although it is also possible that enough Mo for plant requirements may be transported through systems primarily used for other anions. Depending on plant species, and source of nitrogen supply, the critical deficiency levels of molybdenum vary between 0.1 and 1.0 μg g^{-1} (0.1 and 1.0 ppm) leaf dry weight (Gupta and Lipsett, 1981).

A number of Tc studies have shown that roots tend to accumulate a greater proportion of TcO_4^- than shoots at lower external concentrations than at high ones (Mousny et al., 1979; Cataldo et al., 1989; Dehut et al., 1989; Echevarria et al., 1997). This is also found with Mo concentrations in plants (Marschner, 1995). Further, Masson et al. (1989) reported that, during long-term percolation experiments on a calcareous soil, Mo applied to the soil surface (2 μg–200 μg kg^{-1} soil) increased the soil water migration of Tc, thus revealing a competitive effect between the two anions in the soil. Further work by Masson et al. (1989) found that soil to plant transfer of ^{99}Tc in *Lactuca sativa* was inversely proportional to the soil molybdenum concentration applied. These data indicate that it might be useful to investigate further the role of MoO_4^{2-} nutrition in ^{99}Tc uptake by plants.

4. ^{99}Tc transfer from soil to plants

4.1. Soil to plant transfer factors for Tc

Soil to plant transfer of radionuclides is often quantified using a transfer factor (*TF*) defined as the ratio of the activity concentration in the plant (kBq g^{-1} dry weight plant [C_p]) to the activity concentration in the soil (kBq g^{-1} dry weight soil [C_s]). The *TF* is applied in many current assessment models of Tc behaviour in the environment (Green et al., 1996; Thiessen et al., 1999). A variety of studies have shown that, until toxicity, Tc concentration in leaves tends to increase linearly with respect to supplied concentration, i.e. *TF* is independent of concentration (Lembrechts and Desmet, 1984; Van Loon and Lembrechts, 1984; Murphy and Johnson, 1993; Yanagisawa and Muramatsu, 1993; Thiessen et al., 1999). *TFs* for ^{99}Tc have been reported to span three orders of magnitude from 1–1000 (Echevarria et al., 1997). Laboratory studies using soils uniformly amended with TcO_4^- have resulted in transfer factors ranging from 50 to 1000 (Cataldo et al., 1984). Published values of *TFs* for radionuclides have been compiled by the International Atomic Energy Authority (IAEA, 1994) including many for ^{99}Tc. The IAEA have recommended a maximum *TF* for ^{99}Tc of five in food crops and 20 in pasture vegetation.

Many reported *TF* values were obtained from experiments in which Tc was applied directly to the soil surface as TcO_4^-. Laboratory values are, however, often higher than those from experiments carried out in the field. Green et al. (1995, 1996) performed uptake experiments under field conditions using contaminated land reclaimed

from the sea, where waterlogging would have occurred. They obtained *TF* values of less than 2.0 for leafy green vegetables, onions and legumes. These values are similar to those measured under field conditions by Uchida et al., (2000) who also noted that laboratory values were higher than field values. It seems likely that differences between the laboratory and field might result from prolonged contact between ^{99}Tc and soil in the field, perhaps including periods of anaerobic conditions.

Cataldo et al. (1984) investigated a range of plant species and showed that there are significant differences in *TF*s for ^{99}Tc between species and suggested that those in the families Fabaceae and Brassicaceae are highest. Garland et al. (1983) also reported significant interspecific differences. Broadley et al. (1999) showed that there were significant differences between taxonomic groups in radiocaesium uptake by plants and the data of Cataldo et al. (1984) suggests that ^{99}Tc *TFs* may also be influenced by plant taxonomic position. Overall, despite differences between laboratory and field, and between species, reported *TF*s for ^{99}Tc are high. They can be as high as for any other radionuclide that is a potential contaminant of terrestrial systems (Sheppard and Evenden, 1997; Yanagisawa and Muramatsu, 1997; Wang et al., 2000).

4.2. The dynamics of soil to plant transfer ^{99}Tc

Lembrechts et al. (1985) reported that the TcO_4^- content generally increased in leaves of *Spinacea oleracea* L. during four weeks of exposure. However, the content of older leaves actually stabilised whilst that in younger leaves continued to increase. Yanagisawa and Muramatsu (1993) and Yanagisawa and Muramatsu (1997) reported similar findings for a range of vegetable crops. This concurs with other reports that activity is considerably less in storage organs and reproductive parts than in vegetative parts (Bell et al., 1988; Dehut et al., 1989; Murphy and Johnson, 1993; Thiessen et al., 1999). Many studies have reported that Tc is readily translocated to above ground plant parts in annuals (Mousny et al., 1979; Cataldo et al., 1989; Dehut et al., 1989; Degenkolb et al., 1994; Woodard-Blankenship et al., 1995). Values of 85–93% of total ^{99}Tc taken up being transported to shoot tissues have been reported (Mousny et al., 1979; Sheppard et al., 1983; Lembrechts and Desmet, 1984). The rapid translocation of ^{99}Tc to plant leaves might be explained by the fact that xylem walls are negatively charged and so do not adsorb anions (Mousny et al., 1979; Woodard-Blankenship et al., 1995). This is consistent with reports that have shown that $^{99}TcO_4^-$ is the species transported in the xylem (Garten and Lomax, 1989; Krijger et al., 1999). A significant proportion of $^{99}TcO_4^-$ is reduced a few days after reaching the leaves and numerous studies have elucidated the biochemistry of this process (e.g. Harms et al., 1999b). The reduced Tc species can be chemically toxic to plants, an effect that is significant before radiological toxicity (Bennassar et al., 1991). Reduced species of Tc are not rapidly retranslocated.

The effects of retranslocation or redistribution of ^{99}Tc in perennial plants is less well known. The studies of Garten and Lomax (1989) indicate that, at least in deciduous forests, retranslocation is not a significant process. An important consideration is, however, the recycling in the soil of ^{99}Tc contaminated abscised plant material

(Dehut et al., 1989; Garten and Lomax, 1989). ^{99}Tc recycling to the soil solution depends on microbial processes which might be a limiting factor for further plant uptake in the short term (Dehut et al., 1989; Echevarria et al., 1997; Echevarria et al., 1998). However, Dehut et al. (1989) found that the *TF*s obtained from plants grown on soils contaminated with Tc containing plant residues were of the same order of magnitude as those observed for TcO_4^- deposited directly on the soil. These patterns are expected of an ion that, in annual and biennial plants, is taken up during leaf expansion but not retranslocated from there into late leaves, fruit or roots (Krijger et al., 1999).

5. Discussion

5.1. ^{99}Tc in soils

Under oxidising conditions in near-surface groundwater and soil, the principle chemical species of ^{99}Tc is pertechnetate (TcO_4^-). This is water-soluble, stable over a wide pH range and taken up by plants. It is only under reducing conditions that insoluble Tc species are formed. Compared to many nuclides of radioecological interest, ^{99}Tc is therefore generally considered to be highly available to pedological and biological processes. However, if soils with a high anion exchange capacity (oxisols, andisols), soils with andic properties and soils in which anaerobic conditions dominate (histosols, spodosols) are combined with terrestrial wetlands, ^{99}Tc can be predicted to be poorly available in approaching 35% of soils by surface area. Transient periods of anaerobicity in otherwise aerobic soils, now acknowledged to be important for nitrogen transformations on a global scale (Davidson et al., 2000), may increase the proportion of soils in which ^{99}Tc is poorly available in the long term towards 50%. It will be useful to test this prediction, and its implications for soil to plant transfer factors, because nuclear installations are increasing in areas where soil types are different to those in which many experiments with ^{99}Tc have been carried out.

5.2. ^{99}Tc uptake mechanisms in plants

Tc is not an element that is required by plants and it enters plants using mechanisms in place for essential macro- or micronutrients. Until recently, it was tempting to believe that there was a rather restricted set of specific membrane transport proteins in plants for nutrient ions, one of which perhaps provided an entry point for ^{99}Tc. It is now clear, however, that there are many transport proteins involved in nutrient uptake, including families of proteins associated with the uptake of a single nutrient. Molecular studies also suggest that many transporters are not as specific as was concluded from kinetic studies (Eide et al., 1996; Cohen et al., 1998; Zhou et al., 1998). It is becoming clear that there are numerous transport proteins involved in anion uptake by plants and that a variety of them might be involved in TcO_4^- uptake. Patterns of Tc uptake by plants have some similarity with those of various plant macronutrients (SO_4^{2-}, $H_2PO_4^-$, NO_3^-) and the micronutrient MoO_4^{2-}, and might

be influenced by Cl^- transporters. Cataldo et al. (1983) noted the dependence of ^{99}Tc uptake on external pH, which is to be expected of transport through H^+ co-transporters now known to transport many anions. Molecular studies, in particular those with electrophysiological models and knock-out mutants, such as those of White and Broadley (2000) and Broadley et al. (2001), have been useful in radioecological studies of ^{137}Cs (Shaw, 2001) and are likely to prove so for ^{99}Tc. Interestingly, recent studies of ^{137}Cs and its nutrient analogue K, indicate that even if radioisotopes are close analogues of nutrient ions, the transporters that dominate their transport are not necessarily the same (White and Broadley, 2000; Broadley et al., 2001). The variety of transport proteins through which ^{99}Tc might enter plants perhaps helps to account for previous reports of a variety of competition effects. Research with ^{137}Cs (White and Broadley, 2000; Broadley et al., 2001) demonstrates that in the absence of molecular studies, caution is required in speculating about the mechanisms through which radionuclides enter plants.

5.3. ^{99}Tc transfer from soils to plants

Whatever the underlying mechanism, plants clearly have the ability to take ^{99}Tc up quickly. Its availability in aerobic soil, high *TF*s, translocation to vegetative parts, and the short time in which maximum values are reached indicate a significant potential for entry of ^{99}Tc to food chains from contaminated soils. Sheppard et al. (1983) measured ^{99}Tc removal by plants of up to 93%. Grogan et al., (1986), after measuring uptake into a range of crop species over two successive growing seasons, found that the crops removed the entire spike of TcO_4^- during the first season. Echevarria et al. (1997) reported that 97% of soil applied spikes of TcO_4^- was accumulated in the leaves of ryegrass. These studies clearly indicate that from some soil types at least there is very significant potential for phytoextraction of Tc from soils. The generally high uptake of ^{99}Tc by plants indicates that the selection of specific taxa may not be as important for phytoextraction as it is for other radionuclides (Broadley et al., 1999; Willey et al., 2002). The lack of availability in some soils and long-term decreases in ^{99}Tc availability indicate that phytoextraction systems might not achieve the extraction rates reported from experiments but even with this caveat we suggest that there is greater potential for phytoextraction of ^{99}Tc from contaminated soils than other radionuclides. The remobilisation of ^{99}Tc observed from marine sediments may even provide a mechanism of increasing ^{99}Tc availability, as has proved necessary in establishing other phytoextraction regimes (Meagher, 2000). The number of transport proteins involved in ^{99}Tc uptake may, however, limit the impact of recombinant DNA technologies on phytoextraction using ^{99}Tc.

6. Conclusions

Although ^{99}Tc is rightly considered a radionuclide that is generally available to pedological and biological processes in the environment, it seems likely that those soils in which it is most available have been investigated first using short-term experi-

ments. We conclude that further investigations might show that, on a global scale over the medium to long term, ^{99}Tc is not as available as is often assumed. Nevertheless plants clearly have the ability to remove it rapidly from soils in which it is available and there is existing evidence that it can contaminate foodchains rapidly. We conclude therefore that phytoextraction might be a useful decontamination technology for ^{99}Tc but that there is little immediate scope for genetically manipulating ^{99}Tc uptake rates by plants because is seems that a variety of transport proteins are likely to be involved in its uptake. Testing the validity of these conclusions might improve our understanding of the radioecology of ^{99}Tc in terrestrial ecosystems, aid environmental impact assessments for terrestrial waste repositories and provide a decontamination option for some ^{99}Tc contaminated effluents and soils.

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