59351

3. Ball, J. 1939. Contribution to the geography of Egypt. Government Press, Cairo.
4. Eaton, F. M. 1950. Significance of carbonate in irrigation waters. Soil Sci. 69:123–133.
5. Fathi, A., and F. H. Soliman. 1974. Variations in soluble and insoluble matter after the High Dam. Cairo Bull. Agric. Res. no. 40.
6. Hamdi, H., and A. Fathi. 1959. Contribution to the study of the suspended matter of the Nile. Ann. Agric. Sci. 4:19–24 (Cairo, Egypt).
7. Mitkees, A., B. S. Zikri, M. M. El-Banna, and W. A. Abou-Zeid. 1972. Effect of long term storage of the Nile water on its contents of soluble salts and suspended matter. Agric. Res. Rev. 50:31–41 (Cairo, Egypt).
8. Moustafa, A., A. Geith, A. A. Aziz, and M. Tanius. 1959. Annual study for the Nile water from seven different locations. Agric. Res. Rev. 37:45–55 (Cairo, Egypt).
9. Richards, L. A. (ed.). 1954. Diagnosis and improvement of saline and alkali soils. USDA Handbook no. 60. Chap. 5. p. 69–82.

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Technetium Sources and Behavior in the Environment[1]

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ABSTRACT

Technetium (Tc) may enter the environment as a result of nuclear weapons testing, nuclear power production, nuclear fuel reprocessing, nuclear waste storage, and pharmaceutical use. The isotope ^{99}Tc has a long half-life and relatively high fission yield, and an understanding of its behavior and effects in the environment is essential to complete assessment of the environmental impact of the nuclear fuel cycle. Although little is known of Tc environmental behavior, the aqueous chemistry of Tc is well understood and limited laboratory investigations have been conducted on its behavior in soils, plants, and waters. On the basis of this current knowledge, the behavior and implications of Tc in the environment are assessed and avenues of research are suggested.

The most stable chemical species of Tc in aqueous solution is the pertechnetate ion, TcO_4^-. As the pertechnetate ion, Tc is highly soluble in water and in soil, but reduced forms (dioxide and sulfide) have limited solubility; sorption is significant in surface soils of high organic C content and low pH and may be significant in subsoils and geologic media under reduced conditions. A fraction of the sorption measured in surface soils may also have been due to immobilization in microbial cells. The pertechnetate ion is readily available to microbiota, algae, and higher plants and is toxic to higher plants at relatively low soil levels (0.1 μg/g). In higher plants, it is transported largely as the pertechnetate ion and toxicity appears to be due to biochemical rather than radiation effects. Uptake and toxicity appear to be due to Tc functioning as a nutrient analog. Preliminary studies indicate that, in contrast to hydrolyzable radionuclides, incorporation of Tc in plants reduces Tc absorption in animals.

Ultimately, the mobility and availability of Tc to biota will be governed by the quantity and form emitted and its form and solubility over the long-term in soils, sediments, and waters. Uptake by biota will be dependent upon the rate and extent of Tc movement across biological membranes and its toxicity. Proper evaluation of these phenomena will be largely dependent on development of an understanding of Tc sorption mechanisms in soils and sediments and the determination of the stable forms of soluble chemical species that occur in the environment over the long term.

Additional Index Words: **nuclear reactors, nuclear waste, soils, sediments, water, plants, algae, animals, pertechnetate, mobility, availability.**

The environmental behavior of long-lived isotopes resulting from nuclear power generation will be an important factor influencing present-day decisions on nuclear strategy. Of these elements, Sr, Cs, I, Pu, and Am have been receiving intensive study (Cataldo et al., 1978; Francis et al., 1975; White and Dunaway, 1977; Wildung and Garland, 1977). Less is known of the environmental behavior of Tc. Although ^{99}Tc has a long half-life (2.15×10^5 year) and a fission yield approximately equivalent to ^{90}Sr or ^{137}Cs, there are few measurements of its concentration in the environment (Kenna, 1962; Brown, 1967; Attrep et al., 1971; Moss, 1973; Sodd et al., 1975; Birks, 1975; Ehrhardt and Attrep, 1978). This results largely from the difficulties in complete separation of ^{99}Tc, a beta emitter, from shorter half-life Ru isotopes which serve as interferences in direct counting methods. Neutron activation methods have been developed (Foti et al., 1972a, 1972b) to determine Tc at environmental levels but the application of this method has not been reported.

The high fission yield and long half-life of ^{99}Tc insure its presence in the environment at concentrations considerably higher than ^{129}I as a result of worldwide nuclear testing. In addition to fallout levels, the potential also exists for Tc entrance into the environment as a result of nuclear power generation, nuclear fuel reprocessing, nuclear waste storage, and the operation of other facilities, such as hospitals, which use Tc for commercial purposes. When administered to the human body as the pertechnetate ion (TcO_4^-), Tc tends to localize in stomach, salivary glands, and thyroid (Atkins, 1970) and soluble forms of Tc are accumulated by plants (Wildung et al., 1974a, 1977; Gast, 1975). For these reasons, the element is receiving increasing attention in assessment of the impacts of the nuclear fuel cycle (Burkholder et al., 1975).

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The purpose of this review is to summarize current knowledge of the behavior and implications of Tc in the environment and, on the basis of this information, suggest avenues of research that would most expeditiously lead to an understanding of the degree of engineering attention required for Tc in nuclear waste management.

ENVIRONMENTAL BEHAVIOR

The behavior and effects of Tc in the environment are largely governed by its source, its chemistry in soils, sediment and water, and its biological interactions. A great deal is known of the sources and of the aqueous chemistry of Tc relative to the other factors, and this serves as a valuable basis for prediction of the behavior of Tc in the environment. The limited information that is available regarding environmental behavior may then be employed to partially substantiate these predictions.

Sources to the Environment

Technetium is present in the environment principally as a result of natural decay processes, fallout from atomic weapons testing, uranium enrichment facilities, nuclear waste operations, and disposal after pharmaceutical use. Spontaneous fission of ^{238}U in natural ores results in a fission yield of 6.3% for ^{99}Tc (Kotegov et al., 1968; Anders, 1960) with a much smaller contribution from slow neutron-induced fission of ^{235}U. Fission of ^{235}U in a reactor results in Tc isotopes decreasing in yield from 6.1 to 0.2% through the mass series, 97 to 107 (Katcoff, 1958). Technetium does not have a stable isotope. The heaviest isotopes are commonly formed during fission of U, Th, or Pu (Kotegov et al., 1968). Fission of ^{233}U, ^{232}Th, and ^{239}Pu produces high yields of ^{99}Tc (Katcoff, 1958). Technetium is also produced by irradiation of Mo, Nb, and Ru, or by cosmic ray interaction with Mo or Ru (Kotegov et al., 1968; Boyd, 1959). High yields of short-lived isotopes for commercial purposes are obtained using a target of U rather than Mo (Anders, 1960).

There is little published information on fallout from nuclear weapons testing as a source of Tc to the environment. Limited measurements of Tc concentrations in rainfall revealed concentrations ranging from 0.08 to 1.0 pg/liter (Attrep et al., 1971; Ehrhardt and Attrep, 1978). However, information is available on fallout of other long-lived elements. Assuming equivalent retention and deposition of fission products, an estimate of ^{99}Tc concentration in soil can be calculated from relative fission yields and the measured levels of ^{90}Sr and ^{137}Cs in soil that were reported by Hardy (1972). The ^{99}Tc levels in soil (25 cm depth) estimated in this manner amount to 0.01 pg/g soil.

Increases in the use of nuclear power will result in the production of Tc along with other fission products. World inventory of Tc was predicted to exceed 10,000 kg by 1980 (Kotegov et al., 1968). Inventories of ^{99}Tc in the United States were more recently estimated at 1.69×10^5 kg or 2.86×10^6 Ci by the year 2000 (Burkholder et al., 1975). Entrance of Tc into the environment from nuclear power generation may occur as a result of disposal of aqueous wastes from nuclear facilities or during separation and recovery of spent nuclear fuels. At the Diablo Canyon Power Station (San Luis Obispo County, Calif.), 37% of the total annual liquid waste activity expected to be released in the condenser cooling water is attributed to ^{99}Mo, parent nuclide of ^{99}Tc, although the expected release of 2.64 Ci/year ^{99}Mo would represent only about 95 nCi/year ^{99}Tc (Pacific, 1971).

Volatile Tc compounds have some potential for release to the environment during nuclear fuel reprocessing to separate U and Pu. Fuels processing using the gaseous diffusion process may result in the formation of highly volatile TcF_6 and its escape was demonstrated at a molten salt-F volatility plant (Carr et al., 1971). The TcF_6 can be separated from volatile UF_6 by adsorption on MgF_2 (Kotegov et al., 1968). Liquid wastes from other types of reprocessing may also contain Tc which may be disposed to the ground. The Purex and Redox liquid extraction processes have been employed for reprocessing of most of the nuclear wastes to date. In the standard Purex process (tributyl phosphate and kerosene extractions of U and Pu), it is estimated that approximately 20% of the Tc produced in fuel elements remains in the separated U fraction, less than 1% follows the Pu separation, and 70–80% (40 mg/liter) remains in the highly alkaline fission product raffinate which is disposed to waste cribs. There is a possibility it may be coprecipitated in Cs recovery operations, but precipitation during the process or in waste tanks is not expected (Roberts, 1971; Campbell, 1961). Typical waste solutions (Boyd, 1959) from the Redox nuclear fuels reprocessing plant (hexone extraction of U and Pu) contain Tc at levels of 7 mg/liter. The principal differences in Tc concentration in wastes from the Purex and Redox processes likely result from differences in fuels employed and waste treatment (concentration, denitrification), not the extraction process. There have been only limited (unpublished) attempts to isolate Tc from wastes produced by these processes.

Volatile forms of Tc, if released from the dissolver solutions, would likely be Tc_2O_7 or $HTcO_4$ since the formation of stable alkyl reaction products as occurs with I has not been demonstrated and appears unlikely. The gas scrubbers on the stack would, therefore, be expected to strip a major fraction of the Tc from the air stream, as the reaction of Tc_2O_7 or $HTcO_4$ with water in the presence of an oxidizer (i.e., NO_3^-, NO_2^-) would result in nonvolatile pertechnetate. Thus, the majority of the Tc would likely be removed in the condensate or gas scrubbers and discharged to waste cribs.

Use of ^{99m}Tc in pharmaceuticals has increased markedly since its introduction in 1962 (Harper et al., 1962). The isotope has a 6.1-hour half-life allowing administration of quantities sufficient for imaging while minimizing radiation dose. It decays primarily by a single medium-energy photon (140 keV) with 9% internal conversion and virtual absence of dose-contributing beta emissions. The use of ^{99}Mo-^{99m}Tc generators greatly increase the availability of ^{99m}Tc, and selective complexation enables the scanning of specific body organs or systems (Atkins, 1970). The expanding

scope of medical applications on record (Stemple, 1973) attests to the usefulness and multidiversity of the isotope.

Aqueous Chemistry

The chemistry of Tc was the subject of several reviews (Kenna, 1962; Kotegov et al., 1968; Boyd, 1959; Rulfs et al., 1967; Anders, 1960; Cobble, 1964; Korkisch, 1969). A group VII element, Tc most closely resembles Re and, to a lesser extent, Mn. The pertechnetate ion, TcO_4^-, is a weaker oxidant than permanganate, but stronger than perrhenate. Unlike Tc and Re, Mn may form high spin complexes with saturated ligands and, therefore, differs considerably in complex chemistry. The ionic radii of Tc (VII) and Re (VII) at 0.56 Å (Korkisch, 1969) differ considerably from that of Mn (VII), which is 0.46 Å. Differences in redox properties and volatility allow chemical separation of Tc and Re.

Technetium is known to exist in all valence states from +7 to −1, of which the most stable are +7, +4, and 0. Technetium heptoxide, Tc_2O_7, is highly soluble in aqueous solution, forming technetic acid. Both Tc_2O_7 and $HTcO_4$ exhibit considerable vapor pressure as solids or in solution (Cobble, 1964; Cobble et al., 1953). Other volatile forms of Tc include TcF_6 (Selig et al., 1961), $TcCl_6$ (Colton, 1962), and Tc_2S_7 (Perrier and Segre, 1939) and, as noted, these represent possible sources of volatiles to the environment during nuclear fuel reprocessing. Two sulfides may be formed, Tc_2S_7 or TcS_2 (Kotegov et al., 1968). Both are largely insoluble, representing potential chemical repositories in environments where Eh is low and sufficient free S^- is present. Further study is required to determine the conditions necessary for formation of reduced forms of Tc in the environment.

The pertechnetate ion is highly stable over a broad pH range and at concentrations of 1.1×10^{-5} to 0.18*M*. It is likely the most stable chemical species in aqueous solutions, perhaps including natural waters. However, in aqueous solutions, pertechnetate is known to be reduced by Zn and HCl, hydrazine, hydroxylamine, ascorbic acid, $SnCl_2$, and dilute H_2SO_4 to form the hydrated dioxide $TcO_2 \cdot 2H_2O$, although complete reduction to Tc (IV) may be slow (Anders, 1960). It is known that in concentrated solutions pertechnetate may be reduced by dust or organic vapors (Kotegov et al., 1968; Rulfs et al., 1967). The presence of thiourea (Kotegov et al., 1968) results in incomplete reduction to a state believed to be Tc (V). The Tc (V) and also Tc (VI) undergo disproportionation to Tc (IV) and Tc (VII) (Kotegov et al., 1968; Cobble, 1964). The order of hydrolysis of Tc oxidation states is expected to be IV > II > V and VI > VII. Aqueous forms of Tc (IV) may be reoxidized to varying degrees by H_2O_2, bromine water, Ce (IV) ions, HNO_3, MnO_4^-, Cl_2, or air. Tentatively, it would appear that the chemistry of Tc (VII) would govern the behavior of Tc under aerobic conditions. However, the presence of simple inorganic or organic substances and a change in redox conditions in natural systems may markedly influence Tc valence state.

Technetium has a strong tendency to complex in the lower oxidation states (Kotegov et al., 1968). Technetium complexes are expected to be low spin, with the relative stability order for spin-paired complexes determined theoretically as d^1, $d^2 \gg d^5 > d^4 > d^3 > d^6$ (Basolo and Pearson, 1967), which for Tc corresponds to valence VI, V ≫ II > III > IV > I. Ligand type and configuration about the metal will also influence the relative stability. The stability of Tc (IV) complexes is the basis for much of the value of Tc as a pharmaceutical agent. A complexing agent may be chosen to concentrate Tc in specific organs or body systems (Atkins, 1970). Both Tc (V) and Tc (VI) are expected to form highly labile complexes and easily disproportionate in aqueous solution. Complexes of lower oxidation states, of less importance in environmental studies, have been characterized (Kotegov et al., 1968; Armstrong, 1975). Again, it is apparent that, depending upon redox conditions, the presence of complexing agents as occur in natural systems may markedly influence Tc solubility and form. An indication of the possible environmental mechanisms of complexation may be derived from studies of processes for Tc industrial separation.

Solvent extraction of Tc requires the presence of an electron donor basic atom and is favored by a high dielectric constant of the extracting species. The extraction of Tc (VII) increases with increasing O/C atom ratio of the extracting agent, particularly with increasing polar group concentration. A proposed mechanism for extraction is the formation of an ion association pair or cluster involving a cationic complex in the organic phase and an essentially unsolvated TcO_4^- (Boyd and Larson, 1960).

Aromatic substituted or cyclic aliphatic compounds are better extractants of Tc than n-aliphatic compounds. Aliphatic branching near an active group often hinders extraction. Alcohols and amines extract pertechnetate in the order 3° > 2° > 1°. Ketones generally are better extractants than the corresponding alcohols. Organophosphorus compounds extract Tc in order of their relative basicity. Extractability with polyalcohols is dependent on both functional groups and sterochemistry (Richards and Steigman, 1974). Thus, in general, molecules containing functional groups of highest polarity and positive charge may be expected to retain pertechnetate in highest concentrations. The highly polar fulvate and humate fractions and the oxidic Fe and Al fraction that contribute some positive charge in soils and sediments may, therefore, be expected to play a role in Tc retention.

Ion exchange of Tc was extensively studied for industrial purposes (Kotegov et al., 1968; Anders, 1960; Korkisch, 1969). The pertechnetate ion binds strongly to positively charged resins, while reduced forms tend to elute. Pertechnetate would not be expected to sorb in major quantities on the largely anionic colloids in natural waters or soils.

Behavior in Soils, Sediments, and Waters

From a consideration of the sources and aqueous chemistry of Tc, it would appear that Tc would exist predominantly as the pertechnetate ion (TcO_4^-) in aqueous solutions which do not contain strong reducing agents. This would encompass the conditions of many

aerobic agricultural soils and natural waters of the world. The pertechnetate ion is highly soluble and would likely not be sorbed in significant quantities on soils and suspended bottom sediments of predominantly negative charge. From this information, Tc might be predicted to be highly mobile in the soils and waters and available for uptake by biota if biological discrimination did not occur. However, there are several mitigating factors that must be considered including the influence of the source term, soil and water environment, and microbial activity.

Influence of Source—The quantity and form of Tc that may enter the environment as a result of the nuclear fuel cycle are unknown. As discussed above, the sources may be, in part, insoluble, such as certain oxides, and the kinetics of conversion to thermodynamically more stable, soluble forms on entrance into the environment may be slow, depending upon the stability of the oxide to weathering in soil.

Soils and Sediments—Information is available suggesting that Tc from certain sources may be mobile in the environment, but that physicochemical, biological, and time factors may be important in reducing mobility. The Kd values (pCi sorbed per g soil/pCi solute per ml equilibrating solution) for trace quantities (in 0.01*M* $CaCl_2$) of pertechnetate equilibrated for 24 hours under aerobic conditions ranged from 0.007 to 2.8, generally lower than iodide or methyliodide, indicating high mobility (Wildung et al., 1974b). The sorption studies encompassed 22 soils, representing a broad range in physicochemical properties. Sorption that occurred was directly correlated with increased organic C content and inversely correlated with decreased pH. Thus, retention appeared to be closely related to the positive charge on the organic fraction (and perhaps the amorphous, oxidic Fe and Al fraction) which may be expected to decrease with increasing soil pH. In contrast, 8 of 11 surface soils used in another study sorbed 98% of pertechnetate from solution over a period of 2 to 5 weeks (Landa et al., 1977b). This experiment was conducted in a closed unbuffered dialysis system which likely led to anaerobic conditions. Soils that did not exhibit sorption were relatively low in organic C and clay content. A reducing environment may result in formation of highly insoluble $TcO_2 \cdot 2H_2O$ or sulfides or coprecipitation of Tc (IV) with other insolubles such as Fe sulfides. The S content of the soils was not reported in the latter studies. Furthermore, when the experiment was repeated on several of the soils under aerobic conditions, sorption occurred, but not to the same extent and at a slower rate. Thus, as predicted from its basic chemistry, redox conditions may be important in influencing Tc solubility in soil. Surface agricultural soils are not generally anaerobic for extended periods and the importance of this effect will depend on soil type, topography, climatic conditions, and agricultural use as well as the kinetics of mobilization/immobilization. However, aquatic sediments often are anaerobic and may contain elevated levels of S and, therefore, have potential for serving as repositories of Tc. Under aerobic conditions, equilibration of pertechnetate with Pacific Ocean sediment types indicated limited sorption as the pertechnetate ion and no evidence of alteration of the pertechnetate species in solution (Gromov and Spitsyn, 1974, 1975; Gromov, 1974).

Complexation of Tc might be expected to influence Tc mobility in soils and sediments. Low molecular weight complexes may serve to increase the stability of Tc in solution whereas complexation reactions with the insoluble soil organic fraction may lead to immobilization. Technetium (IV) was shown to complex with alcohols (Boyd and Larson, 1960) and polyalcohols (Richards and Steigman, 1974). Tc-tetracyline was shown to bind irreversibly to proteins (Dewanjee and Prince, 1974). Initial investigations (Wildung et al., 1974b), which implicated the soil organic fraction in immobilization, were conducted over a sufficiently short time period that sorption was likely due to chemical interaction with the organic fraction rather than uptake by microorganisms. A lack of sorption by low organic matter soils, reduction in sorption following H_2O_2 digestion of soil, and recovery of sorbed Tc by NaOH extraction also implicated the organic fraction in sorption (Landa et al., 1977b). In the latter study, equilibrations were conducted over longer periods and the soil microflora may have been an important factor. From the known aqueous chemistry, which indicates that Tc is reduced in the presence of organics such as ascorbic acid, and the results of the soils studies, it is likely that the soil organic fraction will play a role in immobilization of Tc, either through sorption by ionic exchange mechanisms, reduction to less soluble forms, or complexation.

Investigation of temperature effects and sterilization on sorption of Tc by several soils (Landa et al., 1977b) implicated the soil microflora in Tc retention by soils. However, the mechanism of retention is not known. Simple uptake by the soil microflora could have accounted for measured sorption; however, the soil microflora may have been responsible for direct reduction of Tc (VII) to Tc (IV) or indirect reduction by utilization of available O_2, either of which might result in increased sorption with time. If microbial uptake is a factor, consideration must be given to Tc solubilization on turnover of microbial tissues. Investigations of these factors, similar to those directed by agricultural scientists toward N and Mn over the years, are required to resolve the mechanisms involved in sorption and the extent of sorption with time as these influence Tc plant availability and entrance into ground and surface waters.

Ground and Surface Waters—Evidence is available suggesting that at least a portion of the Tc released to the environment remains as a soluble species. Technetium was detected by counting methods in ground waters beneath deep sediments underlying the Hanford nuclear waste storage facilities (Brown, 1967). The concentration in the ground water was approximately equivalent to the concentration in the waste stream indicating that, in contrast to most of the radionuclides in the waste, Tc was mobile in soil. This may result from the presence of Tc as the soluble pertechnetate ion or as a soluble complexed species. Evidence supporting pertechnetate as the soluble species includes Tc solubility in alkaline wastes at Hanford, the stability

of the pertechnetate ion in solution, and the low organic C content and likely absence of microbial activity in the deep sediments.

Technetium in ground water exceeded the 0.5-pCi/liter ^{99}Tc detection limit in 20% of weekly ground water samples tested over a 3-year Illinois study (Golchert and Sedlet, 1969). Of that fraction, the average detected ^{99}Tc level was 4.65 pCi/liter for a range of 0.5 to 49.4 pCi/liter. Medical uses have resulted in detectible levels of ^{99m}Tc in several sewer effluents. A 1969–1971 study of 21 hospitals in Allegheney County, Pennsylvania (Moss, 1973) showed an annual increase of 10 to 15% in use of ^{99m}Tc. The estimated concentration of ^{99m}Tc in the effluent sewer stream entering the Ohio River was 1 to 4 pCi/liter. At that time, the ^{131}I contribution was considerably greater than that of ^{99m}Tc. In marked contrast, a 1973 study of 10 Cincinnati hospitals (Sodd et al., 1975) showed 1,900 mCi ^{99m}Tc compared to 10 to 20 mCi ^{131}I administered per week. An estimated 300 mCi ^{99m}Tc reached the Ohio River each week, a value highly variable due to the long sampling times compared to the short half-life of ^{99m}Tc. Each curie of ^{99m}Tc decays to 3 nCi ^{99}Tc, so the resulting yearly contribution to the Ohio River at the time of the study was 47 nCi, a small but increasing, relatively unmonitored source of Tc to the environment.

BIOLOGICAL INTERACTIONS

Ultimately, the availability of Tc to biota will be governed by the quantity and form emitted and its solubility in soils and waters; however, its uptake by biota will also be dependent upon the rate and extent of its movement across biological membranes and its toxicity. There is a rapidly developing body of literature indicating that Tc initially supplied as the pertechnetate ion is accumulated by biota.

Technetium as the pertechnetate ion is readily taken up by soybeans and wheat at soil concentrations of 0.01 to 0.1 μg/g (Wildung et al., 1976, 1977) and at nutrient solution levels as low as 0.02 pg/ml (Cataldo et al., 1978). Marked increases in uptake occurred with increased soil concentration. At soil concentrations below 0.1 μg/g, plants effectively removed up to 90% of the Tc from soil, indicating plant affinities exceeding other nonnutrient nuclides arising from the nuclear fuel cycle. Similar uptake by wheat occurred when Tc was applied as pertechnetate in irrigation waters (Landa et al., 1977a). Soybean plants exhibited Tc localization in stem and leaf tissues immediately after exposure. After 3 weeks, Tc concentration had decreased in stems and increased in leaf, pod, and seed tissues (Cataldo et al., 1976). Plants grown on soils containing Tc levels above 0.1 μg/g exhibited marked toxicity symptoms and presumptive evidence suggested that this was due to biochemical rather than radiation toxicity (Wildung et al., 1975, 1977). The rate of uptake by intact plants was multiphasic over a 0.01- to 10-μm concentration range, suggesting active uptake and specificity for Tc. Several nutrient ions in solution were effective in reducing Tc uptake, including $H_2PO_4^-$, SO_4^{2-}, and MoO_4^{2-}, indicating that similar uptake mechanisms were involved and that toxicity may be due to Tc substitution for a nutrient element and subsequent inactivation of an essential plant process. Chemical studies (Cataldo et al., 1976, 1978) indicated the xylem mobile form in the plant was pertechnetate.

Uptake has also been demonstrated for aquatic biota. The presence of Tc (supplied as pertechnetate) in sea water resulted in whole-body concentration factors of 135 to 205 for red abalone (Spies, 1975). Marine algae exhibited concentration factors in excess of 10^4 (Birks, 1975). Other studies do not generally support accumulation by algae (Gromov and Spitsyn, 1975; Gearing et al., 1971, 1975), but subsequent studies with plants (Cataldo et al., 1978; Wildung et al., 1975, 1977) and microorganisms (Gearing et al., 1975; Garland, unpublished) indicate that the relatively high (μg/ml) levels of ^{99}Tc used in several of the early studies may have been sufficiently toxic to interfere with uptake.

A recent study (Sullivan et al., 1978) compared the gut absorption (rats, Guinea pigs) of Tc incorporated in soybean plants (Tc supplied to plants as pertechnetate in hydroponic cultures) with Tc supplied as pertechnetate in spiked soybean tissues (unincorporated) and in aqueous solution. Approximately 90% of the dose was excreted regardless of the form of Tc administered. Significantly, however, unincorporated Tc excretion was divided equally between urine and feces, whereas plant-incorporated Tc was excreted largely in the feces. Thus, the quantity which was absorbed was considerably greater when Tc was not incorporated. This may result from associations of Tc with larger molecules in the plant tissues, reducing transport across the gut. In this respect, Tc would differ from hydrolyzable metals such as Pu (Wildung and Garland, 1977) which may increase in availability on incorporation into plant tissues.

In all other environmental and biological studies to date, Tc was initially supplied as the pertechnetate ion. Pertechnetate appears quite stable in most of these systems and may be the mobile form in terrestrial plants. However, it is clear from an assessment of the basic chemistry and the results of environmental and animal feeding studies that the principal factors controlling Tc availability to biota, i.e., the quantity and form emitted to the environment and solubility and form in the environment over the long-term, and in biota, remain to be fully elucidated. This will require that attention be given to Tc sorption mechanisms in soils and sediments over the range of conditions encountered in surface soils and deep geologic media and to the detection and characterization of Tc chemical species in environmental substrates and biota.

LITERATURE CITED

1. Anders, E. 1960. Radiochemistry of technetium. USAEC Rep., NAS-NS-3021. Natl. Tech. Inf. Serv., Springfield, Va.
2. Armstrong, R. A. 1975. Chemistry of technetium in low oxide states. Ph.D. Thesis, Stanford Univ. Univ. Microfilm. (Libr. Congr. Card no. mic. 75-13480).
3. Atkins, H. L. 1970. Pathways of an artificial element in the body. USAEC Rep., BNL-50285. Natl. Tech. Inf. Serv., Springfield, Va.
4. Attrep, M. A., J. A. Enorks, and L. D. Broz. 1971. Atmospheric technetium-99. Environ. Sci. Technol. 5:344–345.
5. Basolo, F., and R. D. Pearson. 1967. Mechanisms of inorganic reactions. 2nd Ed., Chap. 3. John Wiley and Sons, New York.
6. Birks, J. L. 1975. Medical radionuclides in marine environments. Nature 255:621–622.

7. Boyd, G. E. 1959. Technetium and promethium. J. Chem. Educ. 36:3–14.

8. Boyd, G. E., and I. V. Larson. 1960. Solvent extraction of heptavalent technetium. J. Phys. Chem. 64:988–996.

9. Brown, D. J. 1967. Migration characteristics of radionuclides through sediments underlying the Hanford Reservation. *In* Disposal of Radioactive Wastes Into the Ground, Int. Atomic Energy Agency Symp., Vienna, Austria. USAEC Symp. Ser., CONF-670512. Natl. Tech. Inf. Serv., Springfield, Va.

10. Burkholder, H. C., M. O. Cloninger, D. A. Baker, and G. Jansen. 1975. Incentives for partitioning high-level waste. USERDA Rep., BNWL-1927. Natl. Tech. Inf. Serv., Springfield, Va.

11. Campbell, M. H. 1961. Extraction of pertechnetate in a purex process. USAEC Rep., HW-69712. Tech. Inf. Center, Oak Ridge, Tenn.

12. Carr, W. H., J. L. King, F. G. Kitts, W. T. McDuffee, and F. W. Miles. 1971. Molten-salt fluoride volatility pilot plant: recovery of enriched U from Al-clad fuel elements. USAEC Rep., ORNL-4574. Natl. Tech. Inf. Serv., Springfield, Va.

13. Cataldo, D. A., R. E. Wildung, and T. R. Garland. 1976. Accumulation of technetium from soil by plants: II. Potential mechanisms for uptake and toxicity. p. 40–42. *In* USERDA Rep. BNWL-2000 Pt 2. Natl. Tech. Inf. Serv., Springfield, Va.

14. Cataldo, D. A., R. E. Wildung, and T. R. Garland. 1978. Technetium accumulation, fate and behavior in plants. Chap. 28. *In* Proc. of the Environ. Chemistry and Cycling Processes Symp., Augusta, Ga. CONF-760429. Tech. Inf. Center, Oak Ridge, Tenn.

15. Cobble, J. W. 1964. Technetium. p. 407–434. *In* I. M. Kolthoff and J. Elving (ed.). Treatise on analytical chemistry. II: Analytical chemistry of the elements. Interscience, New York.

16. Cobble, J. W., W. T. Smith, and G. E. Boyd. 1953. Thermodynamic properties of technetium and rhenium compounds: II. J. Am. Chem. Soc. 75:5777–5782.

17. Colton, R. 1962. Technetium chlorides. Nature 193:872.

18. Dewanjee, M. K., and E. W. Prince. 1974. Uptake of ^{99m}Tc-tetracycline and the pertechnetate ion. J. Nuc. Med. 15(7):577–581.

19. Ehrhardt, K. C., and M. Attrep, Jr. 1978. Technetium in the atmosphere. Environ. Sci. Technol. 12:55–57.

20. Foti, S., E. Dulucchi, and V. Akamian. 1972a. Determination of picogram amounts of ^{99}Tc by neutron activation analysis. Anal. Chim. Acta. 60:261–268.

21. Foti, S., E. Dulucchi, and V. Akamian. 1972b. Determination of picogram amounts of technetium in environmental samples by neutron activation analysis. Anal. Chim. Acta. 60:269–276.

22. Francis, C.W., S. S. Talmage, and B. B. McMullin. 1975. Radionuclide movement in soils and uptake by plants. A selected, annotated bibliography. ORNL-EIS-75-77. Natl. Tech. Inf. Serv., Springfield, Va.

23. Gast, R. G. 1975. The behavior of technetium-99 in soils and plants. Prog. Rep. COO-2447-1. Univ. of Minnesota, St. Paul.

24. Gearing, P. J., C. Van Baalen, and P. L. Parker. 1971. Response of blue-green algae to technetium. p. 857–865. *In* D. J. Nelson (ed.) Radionuclides in ecosystems. Proc. 3rd Natl. Symp. Radioecology, Vol. 2. CONF-710501-pt 2. Tech. Inf. Center, Oak Ridge, Tenn.

25. Gearing, P., C. Van Baalen, and P. L. Parker. 1975. Biochemical effects of technetium-99-pertechnetate on microorganisms. Plant Phys. 55:240–246.

26. Golchert, N. W., and J. Sedlet. 1969. Radiochemical determination of technetium-99 in environmental water samples. Anal. Chem. 41:669–671.

27. Gromov, V. V. 1974. Investigation of the behavior of microelements in ocean water by the desorption method. Radiokhimiza 16:742–745.

28. Gromov, V. V., and V. I. Spitsyn. 1974. Sorption of ^{239}Pu, ^{106}Ru and ^{99}Tc by bottom sediments of the Pacific Ocean. Radiokhimiza 16:157–162.

29. Gromov, V. V., and V. I. Spitsyn. 1975. Assimilability of Pu, Ru and Tc by phytoplankton. USERDA transl., ORNL-TR-2907. Natl. Tech. Inf. Serv., Springfield, Va. Translated from Dokl. Akad. Nauk SSSR 215(1):214–217.

30. Hardy, E. P., Jr. (ed.). 1972. Health Safety Lab. Environ. Quart. USAEC Rep., HASL-259. Natl. Tech. Inf. Serv., Springfield, Va.

31. Harper, P. V., G. Andros, and K. Lathrup. 1962. Preliminary observations of the use of 6-hr ^{99m}Tc as a tracer in biology and medicine. Argonne Cancer Res. Hospital Semiannu. Rep. to AEC, Sept. 1962. Argonne Natl. Lab., Argonne, Ill. p. 76–78.

32. Katcoff, S. 1958. Fission product yields from U, Th and Pu. Nucleonics 16:78.

33. Kenna, B. T. 1962. The search for technetium in nature. J. Chem. Ed. 39:436–442.

34. Korkisch, J. 1969. Modern methods for separation of rarer metal ions. Permagon Press, New York. p. 504–523.

35. Kotegov, K. V., O. N. Pavlov, and V. P. Shvedor. 1968. Technetium. p. 1–90. *In* Advances in inorganic chemistry and radiochemistry, Vol. II. Academic Press, New York.

36. Landa, E. R., L. J. Hart, and R. G. Gast. 1977a. The uptake and distribution of Tc-99 in higher plants. p. 00–00. *In* Drucker and R. E. Wildung (ed.) Biological implications of metals in the environment. USERDA Symp. Ser., CONF-750959. Natl. Tech. Inf. Serv., Springfield, va.

37. Landa, E. R., L. J. Thorvig, and R. G. Gast. 1977b. Effect of selective dissolution, electrolytes, aeration and sterilization on technetium-99 sorption by soils. J. Environ. Qual. 6:181–187.

38. Moss, C. E. 1973. Control of radioisotope releases to the environment from diagnostic isotope procedures. Health Phys. 25:197–198.

39. Pacific Gas and Electric Co. 1971. Environmental Rep., Diablo Canyon Site, Units 1 and 2. San Luis Obispo County, Calif.

40. Perrier, C., and E. Segre. 1939. Some chemical properties of element 43: II. J. Chem. Phys. 7:155.

41. Richards, P., and J. Steigman. 1974. Chemistry of technetium as applied to radiopharmacy. USAEC Rep., BNL-18435. Natl. Tech. Inf. Serv., Springfield, Va.

42. Roberts, F. P. 1971. Summary of research on Tc, Rh and Pd by Battelle-Northwest. USAEC Rep., BNWL-B-49. Natl. Tech. Inf. Serv., Springfield, Va.

43. Rulfs, C. L., R. A. Pacer, and R. F. Hirsch. 1967. Technetium chemistry, oxidation states and species. J. Inorg. Chem. 29:681.

44. Selig, H., C. L. Chernick, and J. G. Malm. 1961. The preparation and properties of TcF_6. J. Inorg. Nucl. Chem. 19:377.

45. Sodd, V. J., R. J. Velten, and E. L. Saenger. 1975. Concentrations of the medically useful radionuclides Tc-99m and I-131 at a large metropolitan waste water treatment plant. Health Phys. 28:355–359.

46. Spies, R. B. 1975. Uptake of Tc from sea water by Red Abalone. Health Phys. 29:695–699.

47. Stemple, R. M. 1973. Bibliography of medical users of technetium-99m 1965–1971. ORAU-121. Natl. Tech. Inf. Serv., Springfield, Va.

48. Sullivan, M. F., D. A. Cataldo, and R. G. Schreckhise. 1978. Absorption and retention of ingested inorganic and organically bound technetium. p. 71. *In* Proc. of World Fed. of Nucl. Med. and Biol. 2nd Int. Congr., Washington, D.C. 17–21 Sept. 1978. (Libr. Congr. 78-70029).

49. White, M. G., and P. B. Dunaway (ed.). 1977. Transuranics in natural environments. NVO-178. Nevada Appl. Ecol. Group, Las Vegas, Nev.

50. Wildung, R. E., D. A. Cataldo, and T. R. Garland. 1975. Accumulation of Tc from soil by plants. USERDA Rep., BNWL-2000, Part 2, p. 40–42. Natl. Tech. Inf. Serv., Springfield, Va.

51. Wildung, R. E., D. A. Cataldo, and T. R. Garland. 1976. Accumulation of technetium from soil by plants. I. Uptake of technetium from soil by soybeans and wheat. USERDA Rep., BNWL-2000, Part 2. p. 37–39. Natl. Tech. Inf. Serv., Springfield, Va.

52. Wildung, R. E., and T. R. Garland. 1977. The relationship of microbial processes to the fate and behavior of transuranic elements in soils, plants and animals. USERDA Rep., PNL-2416. Natl. Tech. Inf. Serv., Springfield, Va.

53. Wildung, R. E., T. R. Garland, and D. A. Cataldo. 1974a. Preliminary studies on the uptake of technetium by soybeans. USERDA Rep., BNWL-1950, Part 2, p. 41–43. Natl. Tech. Inf. Serv., Springfield, Va.

54. Wildung, R. E., T. R. Garland, and D. A. Cataldo. 1977. Accumulation of technetium from soil by plants. Health Phys. 32(4):314–317.

55. Wildung, R. E., R. C. Routson, R. J. Serne, and T. R. Garland. 1974b. Pertechnetate, iodide and methyl iodide retention by surface soils. USERDA Rep., BNWL-1950, Part 2, p. 37–41. Natl. Tech. Inf. Serv., Springfield, Va.