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Behavior of Technetium in Soil: Sorption-Desorption Processes

J. Henrot
C. T. Garten, Jr.
B. G. Blaylock

Environmental Sciences Division
Publication No. 3072

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ENVIRONMENTAL SCIENCES DIVISION

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J. Henrot
C. T. Garten, Jr.
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Environmental Sciences Division
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*Submitted as a thesis by Jacqueline Henrot to the Graduate Council of The University of Tennessee, Knoxville, in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

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ABSTRACT

Technetium-99 (^{99}Tc) is a long-lived radionuclide (half-life of 2.1×10^5 years) produced by nuclear industries. In case of release, its likely form in the environment is the pertechnetate anion TcO_4^-. The behavior of TcO_4^- in soil is important to assess Tc short-term and long-term geomobility and plant availability. Behavior of Tc in soil has been the object of many studies, however, results of laboratory experiments, indicating low Tc sorption in soil, conflict with the observed behavior of Tc in the field (high sorption and reduction of the soil to plant transfer factor with time). Microbial activity has been suggested to play a role in Tc sorption; however, the process involved and the extent of the bacterial involvement are unknown.

The objectives of the first part of this thesis are to determine if soil bacteria affect TcO_4^-, and if so, by which mechanism. Bioaccumulation of Tc and chemical modification of TcO_4^- were studied in mixed cultures of aerobic and anaerobic soil bacteria, and in pure culture of sulfate-reducing bacteria. Bacteria were grown in liquid media and Tc association with organics was determined by gel permeation chromatography. Mixed aerobic bacteria had no apparent effect on TcO_4^-. Mixed anaerobic bacteria reduced TcO_4^-, enabling its association with the organics of the growth medium. Reduction was a metabolic process and not merely the result of reducing conditions. Sulfate-reducing bacteria efficiently removed Tc from solution (up to 70% of the total Tc was bioaccumulated and/or precipitated as Tc-sulfide) and promoted its association with organics. Pertechnetate was not reduced by the same mechanism as dissimilatory sulfate reduction but by a reducing agent released in the growth medium. Technetium associated with bacterial polysaccharides only in the anaerobic cultures.

The second part of the thesis has for objectives to (1) provide data on the kinetics and the extent of Tc sorption and desorption under conditions realistic for the field, (2) determine the importance of microbial activity, soil water content, Tc concentration, and organic matter on Tc sorption, and (3) describe the behavior of Tc under fluctuating water tension. Technetium sorption was studied in 2 contrasting horizons of an Ultisol : Ap horizon (2.73% organic matter, high microbial activity) and Bt horizon (0.51% organic matter, low microbial activity). *Fresh* samples of the 2 horizons were incubated in the laboratory under various soil water contents and Tc concentrations. At time intervals, soil water was collected from the samples by centrifugation and sorption was calculated from the change of Tc concentration in the soil water. Microbial activity was reduced by gamma-irradiation of the soil.

Under all experimental conditions, little sorption took place in the Bt horizon. In the Ap horizon, sorption was rapid (equilibrium was achieved in a few days) and the Tc soil-water equilibrium distribution was primarily a function of the soil water content and microbial activity. A reduction of microbial activity delayed and diminished sorption. As the soil water content increased, Tc sorption augmented. At field capacity, 50% of the Tc was sorbed, whereas under flooded conditions, sorption was complete. As Tc concentration in the soil water increased, the amount of Tc sorbed by Ap at field capacity increased, but the fraction of Tc sorbed decreased. Under flooded conditions, sorption was complete at all concentrations. Mathematical parameters describing Tc sorption as a function of time and Tc equilibrium distribution as a function of Tc concentration are provided in the text.

Organic matter was extracted from contaminated soil samples in 3 successive fractions of increasing pH. Technetium association with these fractions and the soil residue was determined as a function of time and Tc concentration. A large fraction of the Tc sorbed was associated with the soil organic matter indicating that complexation with soil organics was the predominant mechanism of Tc sorption. Technetium

distribution pattern among fractions did not vary with time or Tc concentration : Tc was distributed among fractions proportionally to the amount of functional groups they carried. Consequently, Tc was predominantly associated with the low molecular weight fraction of the soil organic matter. Technetium in the soil water was not associated with soluble organics but remained as TcO_4^-.

Release of Tc from Ap samples upon air-drying was rapid and important; up to 75% of the sorbed Tc was released within a few days. No measurable additional release took place in the following 85 days of the experiment. Under conditions of fluctuating soil water content, an expected sequence of sorption, desorption, and resorption was observed.

In conclusion, the Bt horizon that is poor in organic matter and has a low bacterial population has also a low sorption potential for Tc. The Ap horizon did sorb Tc, the proposed conceptual model of Tc behavior in Ap is that (1) Tc is used by anaerobic soil bacteria as terminal electron acceptor for the respiratory chain and reduced, (2) once reduced, Tc is complexed with the carboxyl groups of the soil organic matter, (3) when oxygen is present in the soil, there is an equilibrium between reduction-complexation and oxidation of Tc that determines the partitioning of Tc between sorbed Tc and TcO_4^-, (4) sorbed Tc is partially released from the Tc-organic matter complexes when the soil air-dries. Technetium behavior in soil is a dynamic process determined primarily by soil type and fluctuations in soil water content.

CHAPTER I

INTRODUCTION

A. Foreword

The use of nuclear energy to generate electricity is increasing and is projected to grow in many countries as they commit themselves economically to fission energy. As a consequence of the developing nuclear industry, we face today an increasing introduction of radioactive material into our environment : discharges from nuclear power plants and reprocessing facilities, leakages from terrestrial and deep-sea disposal sites, and accidental releases.

Exposure of human populations is the principal concern relative to released radioactivity. Direct exposure, principally from inhalation of radionuclides in air, can be large in the case of an accident, however, the greatest risk for the population from routine releases in the operation of nuclear facilities is the intake of contaminated food and water. The evaluation of the quantity of radionuclides potentially present in the human diet requires a knowledge of the magnitude of the radioactivity released and, more importantly, of the pathways of transfer from the site of release to human food items and drinking water.

Radionuclide transfer among ecosystems (e.g., from aquatic to terrestrial systems) and within ecosystems (e.g., through the food chain) obey the same complex biogeochemical processes that govern the cycling of nutrients and the fate of conventional pollutants. Therefore, the elucidation of these processes is not only of interest to radioecology, but is also of general interest for ecology and toxicology.

In terrestrial ecosystems, the fate of radionuclides is predominantly affected by the biogeochemical processes taking place in the soil, as long as direct deposition on vegetation is not an overriding factor. Sorption in

soil determines not only the quantity of radionuclide immobilized, but also the quantity potentially exported (leached from the soil to ground water and aquatic environments) and the quantity available for plant uptake and transport through the food chain. The physico-chemical and biological factors that alter the chemical form of the radionuclide are very important, because chemical form affects radionuclide sorption to the soil, as well as the geochemical mobility and the bioavailability of its non-sorbed species.

The role of bacteria in the immobilization and biomodification of some nutrients is well known. Bacterial metabolism, for example, largely determines the behavior of N and S in soils rich in organic matter. In recent years, much attention has been given to the role of microorganisms in the speciation and sorption of radionuclides in soil (Bonnyns-Van Gelder and Kirchmann, 1984).

The objective of this thesis is to provide a better understanding of the sorption and desorption behavior of technetium (Tc) in soil and to determine the role played by the soil microbial flora, and other non-biological factors, in the sorption process.

Technetium has a special significance among the radionuclides produced by the nuclear industry because of its long half life (2.1×10^5 years), its high levels in nuclear waste, and its environmental release during the uranium fuel cycle.

The chemical form of Tc likely to exist in the environment under oxidizing conditions is the oxy-anion pertechnetate (TcO_4^-). Early studies on TcO_4^- behavior under laboratory conditions had suggested a marked bioaccumulation by plants and a potential for high geochemical mobility (Wildung et al., 1974; Routson et al., 1977; Balogh and Grigal, 1980). Subsequent work, however, indicated that in the field, soil-to-plant transfer factors were lower than expected, and that Tc retention in soil could be quite important (Hoffman et al., 1982a; Garten et al., 1984; Vandecasteele et al., 1986). Furthermore, sorbed Tc was found associated

with the soil organic matter (Bondietti and Garten, 1986; Stalmans et al., 1986). It was clear that TcO_4^- underwent chemical changes in the field. Indications that microbial activity was playing a role in Tc retention accumulated (Landa et al., 1977; Mousny and Myttenaere, 1981). However, the processes involved and the extent of the involvement of bacteria in sorption were unknown. Also unknown were the kinetics of Tc sorption and desorption under field conditions, and the details of the environmental factors affecting the geochemical behavior of Tc in soil.

The objectives of the first part of this thesis are to determine if soil bacteria *per se*, affect TcO_4^-, and if so, by what mechanisms (modification of chemical form, bioaccumulation). The second part seeks to determine the extent of the microbial involvement in Tc sorption and the critical parameters affecting Tc sorption and desorption in soil. The conclusions provide an understanding of the mechanism of Tc sorption and desorption in soil, and consider the implications of Tc behavior in soil for radiological assessment.

B. Source Term of Technetium

Technetium has no stable isotope, and since the half life of its longest lived one (^{98}Tc : 4.2×10^6 years) is largely inferior to the age of the earth, primordial Tc has disappeared. Minute quantities of Tc are produced by the spontaneous fission of ^{238}U and the slow neutron-induced fission of ^{235}U (Anders, 1960; Kotegov et al., 1968; Schowchau, 1983), and are thus present in U ore.

The isotope ^{99}Tc is produced by thermal fission of ^{235}U and ^{239}Pu in nuclear reactors. Its maximum yield from ^{235}U is 6.1%, making it relatively abundant among the fission products (Katcoff, 1958). Due to its very long half life (2.1×10^5 years), ^{99}Tc becomes the predominant radionuclide in spent fuel between 5×10^3 and 1×10^6 years after its discharge from the reactor (Bocola, 1979).

Spent fuel is either disposed of after initial cooling, or is reprocessed, enriched in the fissible isotope ^{235}U, and re-used. Till et al. (1985) calculated the source term of Tc at each stage of the uranium fuel cycle for a pressurized water reactor assuming both the recycling or no recycling options (Fig. I.1). The predominant Tc release to the environment is anticipated from the liquid effluents of uranium enrichment plants processing recycled reactor fuel. The probable chemical form of the release is technetium hexafluoride (TcF_6) gas which hydrolyses rapidly into TcO_4^- (Carlsen et al., 1984), the form detected in the effluents.

Technetium-99m is used in nuclear medicine to label radiopharmaceuticals for organ scintigraphy. This isotope has a short half life (6.1 hours) and decays rapidly into the low energy ^{99}Tc by γ emission (Schwochau, 1983). The source term from nuclear medicine, however, is negligible compared to the releases from the nuclear electricity-generating industry.

The quantity of ^{99}Tc released into the environment from fallout during the nuclear weapon testing period has been estimated (Wildung et al., 1979). This does not contribute significantly to the source term of Tc, especially if one takes into account the fact that releases from nuclear facilities will continue in the future, whereas most above-ground weapon testing was stopped in 1962 (the exceptions are : Chinese test in 1964 and Indian test in 1974).

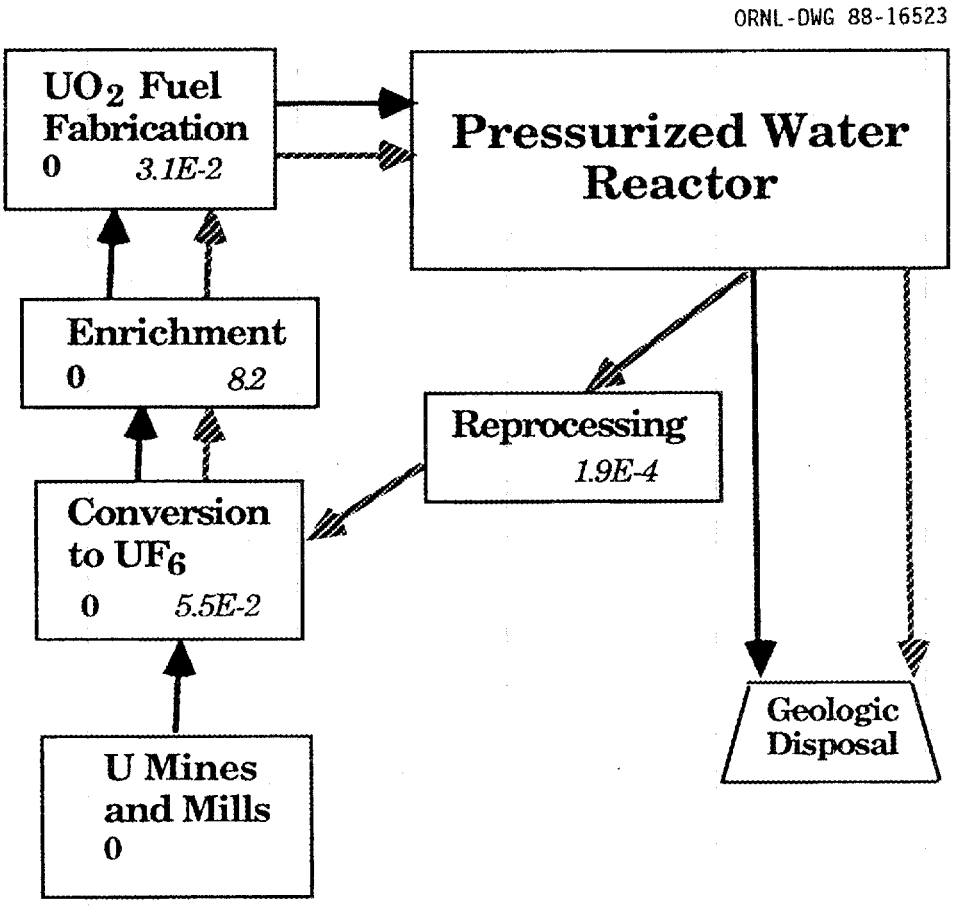

Fig. I.1. Source term of technetium in the uranium fuel cycle. The calculated Tc releases from U fuel cycle without reprocessing of the spent fuel (plain arrows, no Tc released) and with reprocessing of the spent fuel (striped arrows and italic numbers) are given in GBq/reference reactor year; after Till et al. (1985).

C. Physico-Chemical Properties

Technetium-99 is a weak β^- emitter (E_{max} = 0.292 MeV) of low specific activity (0.63 GBq g^{-1}) and long half life (2.1×10^5 years). The nature of its decay and its low specific activity make the detection of ^{99}Tc difficult.

Therefore, the isotope ^{95m}Tc, a γ emittor with a high specific activity (832.5 TBq g^{-1}), is frequently used as a tracer of ^{99}Tc in laboratory and environmental studies.

The chemistry of Tc is dominated by oxidation-reduction reactions and, for the reduced states, by complex formation. Technetium, like the other elements of the group VIIB (Mn and Rhe), exhibits numerous oxidation states. Configurations from -I to +VII are possible.

In aqueous media and in the absence of complexing agents, the most stable oxidation states are +VII and +IV ; the others, less stable, have the tendency to convert themselves into +IV and +VII (Paquette et al., 1980; Schwochau, 1983). The predominance diagram of Tc shows that the pertechnetate anion (TcO_4^-) is stable over a wide range of Eh and pH (Fig. I.2). As the redox potential decreases, insoluble Tc dioxide ($TcO_2.H_2O$) becomes the predominant stable species (Carlsen et al., 1984).

Predicting the chemical form of Tc in the environment from this diagram should be done with extreme caution because : (1) it has been constructed using few experimentally-derived thermodynamic data, some of which are of questionable accuracy (Paquette et al., 1980), and (2) it indicates the thermodynamically stable species, and does not provide information on the kinetics of the transformations.

Reduction to Tc(IV) and reoxidation of TcO_2 are not easily achieved. Chemical reduction of TcO_4^- to lower valences and TcO_2 requires rather drastic conditions. The most frequently used methods are : decomposition

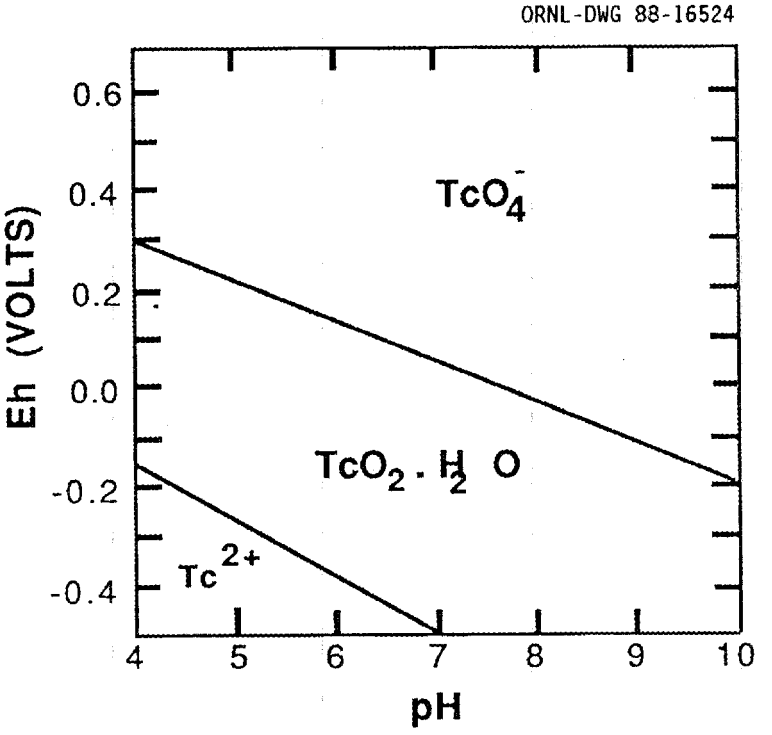

Fig. I.2. Predominance diagram for technetium visualizing the possible Tc-species as a function of Eh and pH. The solid lines denote a 50:50 concentration ratio between the species involved (From Carlsen et al., 1984).

of NH_4TcO_4 in a nitrogen stream at 700 to 800 °C, electrochemical reduction, or reduction with strong reducing agents such as Zn/HCL, Sn^{2+}, hydrazine, borohydride, hydroxylamine, and ascorbic acid. Complete reduction to Tc(IV) with these latter compounds can be slow (Anders, 1960).

Conversely, oxidation of TcO_2 is obtained to varying degrees by strong oxidizing agents such as alkaline peroxide, bromine water, ceric ions, acid persulfate, nitric acid, permanganate, chlorine or air (Anders, 1960). The rate of TcO_2 oxidation upon exposure to air is rather slow, but not well defined. The values reported by Stalmans (1986) (reoxidation half-times from 5 to 120 days) are a function of the nature of the reducing agent used to generate the precipitate.

In view of the difficulty and sluggishness with which Tc is reduced and reoxidized, it is not surprising that, for example, TcO_4^- can be observed in conditions where the Eh/pH diagram predicts the predominance of TcO_2 (Stalmans, 1986; personal observation).

Technetium (VII) does not form complexes, however, in the presence of the appropriate ligand, lower valences of Tc may be stabilized by complex formation, making these oxidation states probable under slightly oxidizing conditions (Carlsen et al., 1984). Organic complexes of ^{99m}Tc are widely used in nuclear medicine as imaging agents for organ scans. Nevertheless, their oxidation state, coordinative structure and overall charge are rarely established, and little is known about their thermodynamic stability (Russel et al., 1980; Russel and Majerik, 1978; Hwang et al., 1984; Muenze et al., 1984). It is generally believed that TcO_4^- is *probably* reduced to a cationic species which are then chelated by the radiopharmaceutical carrier (Eckelman et al., 1971).

Complex formation is obtained with a variety of organics carrying one or a combination of the following functional groups : amino, hydroxyl, carboxyl, and sulfydryl. They can be divided into 4 main

categories : hydroxycarboxylates (citrate, malate, tartrate, gluconate), aminocarboxylates (EDTA, DTPA), polyamines (ethylenediamine, tri-, tetra and pentamines), and sulphydryl amino acids (methionine, cysteine) (Roucoux, 1980; Slifkin and Ellis, 1978; Johannsen et al., 1977). With the exception of polyamines, the most stable configurations are achieved when binding involves different functional groups. Di- and tricarboxylic acids, for example, are unable to stabilize reduced Tc unless at least one adjacent hydroxyl group is present (Grossman and Muenze, 1982). Technetium-complexes with various sugars, nucleotides, nucleosides, and polysaccharides such as starch have also been observed (Paquette, 1980).

In the soil, a wide variety of compounds at different stages of degradation present the combination of functional groups required to complex Tc. Soil polysaccharides and soil organic matter, for example, are likely ligands for reduced Tc. Technetium-soil organic matter complexes have been produced in soil incubated with a chemical reductant, or with a large inoculum of *E. coli* and growth medium (Van Loon et al., 1986b).

Other Tc compounds of environmental significance are the Tc sulfides. Indeed, in the presence of H_2S, Tc(VII) and Tc(IV) can form sparingly soluble compounds : Tc heptasulfide (Tc_2S_7) and Tc disulfide (TcS_2) (Paquette et al., 1980; Anders, 1960; Lee and Bondietti, 1983).

In conclusion, the stable chemical form of Tc under most environmental conditions is likely to be TcO_4^-. Chemical or microbiological processes can reduce Tc to a lower oxidation state. Reduced Tc precipitates as TcO_2 or forms complexes with organic compounds. Hydrogen sulfide insolubilizes Tc as Tc sulfide.

CHAPTER II

MATERIAL AND METHODS

A. Bacterial Cultures (in Chapter III)

1. Technetium isotopes, concentration, and analysis

$Na^{99}TcO_4$ was traced with $Na^{95m}TcO_4$. Technetium-99 concentration in the growth medium was 620 Bq L^{-1} when not indicated otherwise. Technetium analysis was performed on the ^{95m}Tc isotope by gamma counting. Except when indicated otherwise, Tc was added to the growth medium at the same time as the bacterial inoculum.

2. Organisms and their cultivation

Mixed aerobic and anaerobic bacteria

A mixed inoculum was isolated from the top horizon of a forest soil and grown at room temperature in a yeast extract peptone medium (YEP : yeast extract, 0.2 gL^{-1}; peptone, 2 gL^{-1}; dextrose, 1 gL^{-1}; NH_4NO_3, 0.2 gL^{-1}, pH 7). The mixed aerobic bacteria were grown in 250 mL Erlenmeyer flasks containing 50 mL of medium and agitated on a rotary shaker at 120 rpm. The mixed anaerobic bacteria were grown in similar flasks, tightly stoppered and filled to the top to avoid air space; the growth medium was vigorously boiled before use and resazurin (2 mgL^{-1}) was used as a color indicator of anaerobiosis (Costilow, 1981). Pure isolates of aerobic bacteria were obtained from the mixed cultures by successive streaking on YEP agar. Growth of the aerobic bacteria was measured by turbidimetry at 650 nm. Redox potential (Pt/Ag-AgCl electrode) and pH were recorded at the time of sampling. Since the response of the

platinium electrode is pH dependent, the redox potentials shown in Fig. III.1B and III.2B were corrected to pH 7 (Eh_7) by subtracting or adding 0.059 V per pH unit under or above pH 7, respectively.

Sulfate-reducing bacteria

Two strains of sulfate-reducing bacteria : *Desulfovibrio vulgaris* and *D. gigas* (received from the University of Georgia, courtesy of Dr. H. Peck) were grown in 17 mL screw cap test tubes filled with an appropriate growth medium (SOR : yeast extract, 1 gL^{-1}; NH_4Cl, 1 gL^{-1}; K_2HPO_4 , 0.5 gL^{-1}; $MgSO_4.7H_2O$, 2 gL^{-1}; $CaCl_2$, 0.2 gL^{-1}; Na_2SO_4, 4 gL^{-1}; $Fe(NH_4)_2(SO_4)_2$, 0.05 gL^{-1} and 12.5 ml 60% lactate, pH 7.2). Sulfate-reducing bacteria are obligate anaerobes that require a low redox potential to initiate growth (Postgate, 1984). As pertechnetate cannot exist in the presence of the reducing agents commonly used in anaerobic cultures to depress and poise the redox potential at optimum levels (Costilow, 1981), dissolved oxygen was removed from the medium by a cytochrome-based electron transport system isolated from *E. coli* membranes (Adler et al., 1981; Adler et al., 1983). This "membrane fraction" had no effect on pertechnetate (see below).

3. Bioaccumulation

The bacteria were harvested by centrifugation (10,000 g for 10 min.), washed twice with phosphate buffer saline (PBS), dried at 100°C and analysed for Tc. The Tc concentration in the medium was also determined at the time of sampling. Bioaccumulation is expressed as a concentration ratio (CR) : dpm Tc (g bacteria dry weight)$^{-1}$ divided by dpm Tc mL^{-1} medium.

4. Determination of the chemical form of technetium in the growth medium

The association of Tc with organic materials of the growth medium was studied by gel exclusion chromatography on Biogel P2 using 0.15 M NaCl as eluant. The column effluent was collected in 3 mL fractions and analysed for Tc; the elution of organic material was monitored by on-line UV absorption (254 nm). The chromatography column was kept free of dissolved oxygen. Pertechnetate, added to the blank growth media as a control for the effect of both the media and the "membrane fraction", always eluted as pertechnetate.

To differentiate between direct and indirect effects of bacteria on the chemical form of Tc, growth medium aliquots were taken with a syringe from cultures grown in the presence of Tc (direct) or from cultures grown in the absence of Tc (indirect). In the latter case, the aliquots were forced through a 0.22 μm filter fitted to the syringe into a evacuated blood collection tube (Vacutainer Brand, sterile) to which pertechnetate was subsequently added, and the mixture was allowed to equilibrate before being chromatogaphed.

5. Isolation of the capsular (CPS) and exo-polysaccharides (EPS) fractions

The bacterial cultures were centrifuged at 10,000 g for 10 min. The dissolved EPS present in the supernate were precipitated overnight with 3 volumes of 99% ethanol, centrifuged, and washed with 99% ethanol. The bacterial pellet, after 2 washes with PBS, was mixed at high speed with a handmixer in 0.5 M NaCl for 3 min., centrifuged, and the supernate (CPS) was dialysed in a Spectrapor # 3 membrane (3500 daltons

molecular weight cut off) against dinitrogen-saturated distilled water until equilibrium was reached.

B. Soil Experiments (in Chapter IV)

1. Soil characteristics

The soil used in this study is a poorly drained soil (Aquic Hapludult) located on a stream terrace near the Clinch River (Oak Ridge, TN), in an old field cultivated prior to 1943. The soil has A, Ap, AB and Bt horizons. Only the topsoil horizon (Ap) and subsoil horizon (Bt) were sampled. Their characteristics are given in Table II.1.

2. Treatments

Technetium sorption kinetics and equilibrium distribution in soil were studied on samples of the topsoil (Ap) and the subsoil (Bt) under varied conditions : native state or irradiated (i), at field capacity (FC) or under flooded condition (FL). The combination of these conditions yields eight treatments : Ap horizon at field capacity and non-irradiated (**ApFC**), Ap horizon at field capacity and irradiated (**ApFCi**), Bt horizon at field capacity and non-irradiated (**BtFC**), Bt horizon at field capacity and irradiated (**BtFCi**), Ap horizon flooded and non-irradiated (**ApFL**), Ap horizon flooded and irradiated (**ApFLi**), Bt horizon flooded and non-irradiated (**BtFL**), Bt horizon flooded and irradiated (**BtFLi**). To refer to both non-irradiated and irradiated treatments, the symbol & was used (e.g. ApFC&i).

Table II.1. Soils characteristics.

		Ap	Bt
pH in H_2O (1:1)		5.0	5.2
pH in $CaCl_2$ (1:1)		4.5	4.2
% Organic Carbon		1.4	0.2
% Organic Matter[a]		2.7	0.5
Texture		silty loam	silty clay loam
Color		10YR4/3	10YR5/6
Depth		0 to 0.15 m	0.50 to 1.00 m
Characteristics		mottling	mottles 2.5Y6/4
CEC[b] (cmol(+) kg^{-1})		7.2	5.8
% Base Saturation		94.1	68.3
Exchangeable Cations :			
(cmol(+) kg^{-1})	Ca	5.4	3.0
	Mg	1.1	0.8
	Al	0.4	1.8
	K	0.2	0.1
	Na	0.0	0.1
FC (%)[c]		32.9 ± 0.2	23.9 ± 0.3

[a] The percentage of organic matter was calculated by multiplying the percentage of organic carbon by 1.9 and 2.5 for topsoil and subsoil respectively, as recommended in Nelson and Sommers (1982).

[b] The soil cation exchange capacity is expressed as the sum of exchangeable cations.

[c] FC = field capacity, expressed in percent by weight (PW).

3. Soil sample preparation and Tc addition

The soil was used immediately after collection from the field to minimize disturbance to microbial activity. It was screened through a USDA standard testing sieve # 4 with 4.75 mm openings, weighed into field moist equivalents of 17.7 (Ap) and 23.2 (Bt) g oven dry weight, and placed in round polyethylene boxes (56 mL) covered with a thin low density polyethylene film (Fig. II.1.A). The polyethylene film allows oxygen diffusion with little loss of water (Renfrew and Morgan, 1960). Water loss from the samples was linear with time and, at the end of the 30 day period of the experiment, a maximum of 7% of the total soil water had diffused through the film.

Nine milliliters of distilled water were added to the samples destined to be flooded, and they were incubated for 10 days (ApFL, BtFL) or incubated for 10 days then γ irradiated (ApFLi, BtFLi) before the addition of Tc. ApFCi and BtFCi samples were also γ irradiated before Tc contamination. Technetium was added to the samples in an amount of water (Table II.2) calculated to reach the desired water tension for each of the treatments.

To obtain a homogeneous distribution of the small amount of Tc solution added to the samples at field capacity, the soil contained in a polyethylene box was spread on a plastic sheet and the pertechnetate solution was added dropwise with a Pasteur pipette following a grid pattern (Fig. II.1.B). The sample was mixed and replaced in the box. The total operation lasted only a few minutes.

In the case of the flooded samples, the Tc solution was added to the already-flooded soil, and mixed with a glass rod. Irradiated samples were handled as described above but the addition of water and Tc took place in a sterile chamber, inside a plexiglass box, with autoclaved

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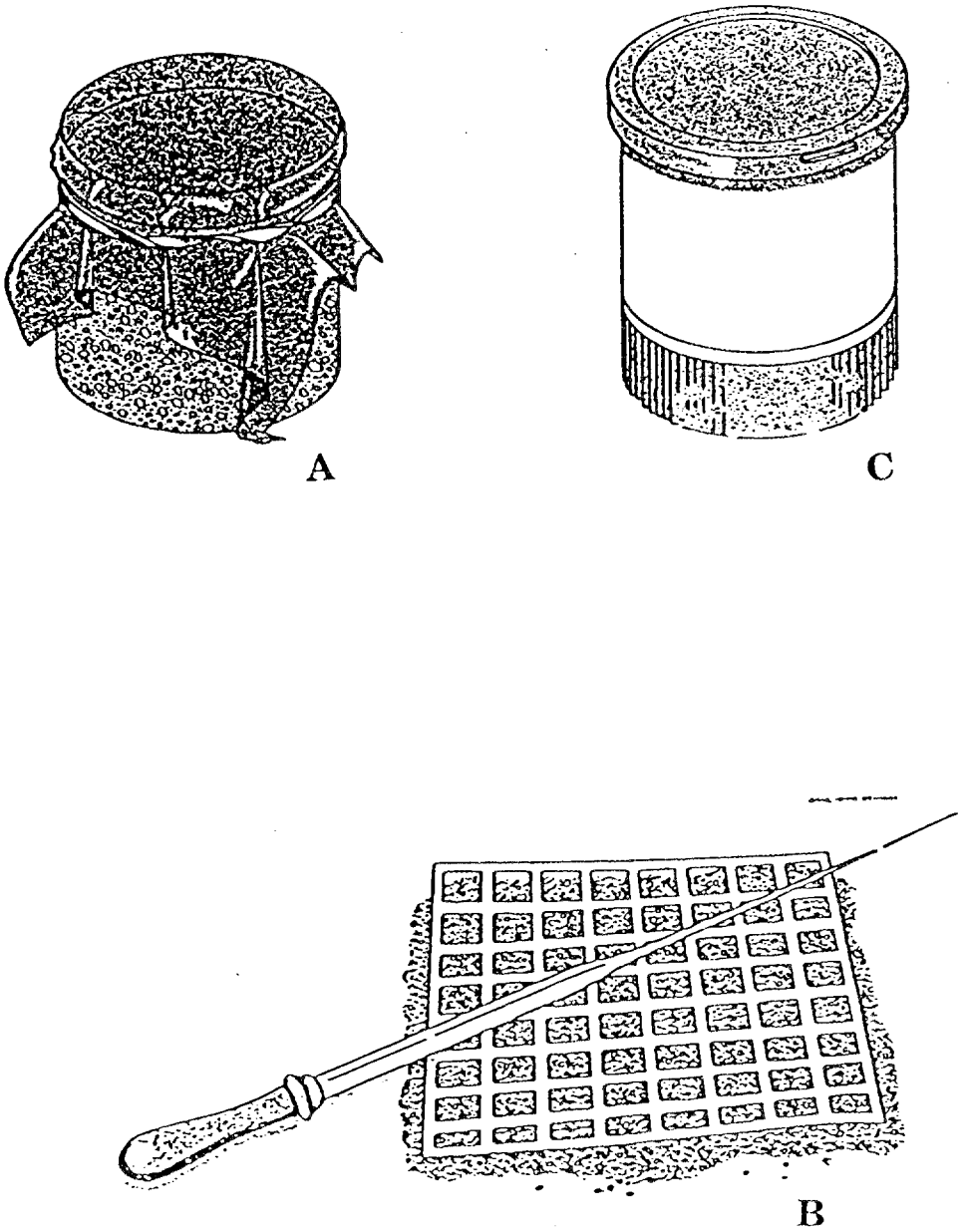

Fig. II.1. Material. (A) Polyethylene box containing a soil sample. (B) Grid used to add Tc homogeneously to the soil sample. (C) Centrifugation assembly.

Table II.2. Original soil water content and water added to the samples of each treatment.

Treatment	Original FW[a] (g)	Oven-dry Weight (g)	Original Soil Water (mL)	Water Added (mL)	Total Soil Water (mL)	Sample FW (g)
ApFC&i	22.8	17.7	5.1	0.9	6.0	23.7
ApFL&i	22.8	17.7	5.1	9+1[b]	15.1	32.8
BtFC&i	27.1	23.2	3.9	1.7	5.6	24.9
BtFL&i	27.1	23.2	3.9	9+2[b]	14.9	34.2

[a] FW for fresh weight
[b] Nine milliliters of water to flood the soil, the remaining added with Tc 10 days afterwards.

equipment and solutions. All samples were incubated in an environmental chamber at 25 ^{o}C during the experiment.

4. Reduction of microbial activity

Gamma irradiation was chosen as a method to decrease the microbial activity in the sample because it is less destructive than other methods to the organic matter and other soil properties (McLaren, 1969; Powlson and Jenkinson, 1976; Ramsay and Bawden, 1983).

Samples placed in a waterproof box were lowered in the cooling pond of the High Flux Isotope Reactor facility (Oak Ridge National Laboratory) and received gamma rays emitted by spent fuel assemblies for seven hours. The gamma field flux was 4.4×10^5 R/h at the entrance in the box and 1.4×10^5 R/h at the exit so that the average gamma flux was considered as 3.0×10^5 rad/h, giving a total accumulated dose of 2.1 Mrads. Two megarad is a dose often reported in the literature as sufficient to suppress microbial activity (Powlson and Jenkinson, 1976; Popenhoe and Eno, 1962; Peterson, 1962; Cawse, 1975; Cawse and Cornfield, 1971).

Replicate plate counts were performed on fresh soil and irradiated samples, using the yeast extract peptone medium described earlier as growth medium. The reduction of bacterial numbers observed was from $2x10^{10}$ to $3x10^{2}$ (3 identical colonies observed on the first dilution plate) and from $2x10^{5}$ to 0 bacteria per gram of soil dry weight for Ap and Bt respectively. The most probable number technique gave similar numbers.

In a ApFLi sample incubated for 30 days, 79 colonies of at least 8 types were observed on the fourth dilution plate, indicating that the microbial population had reached a size of $7.9x10^{6}$ bacteria per gram of soil. Since bacterial spores have a high radioresistance (Hannan, 1955) and spore-forming species of *Bacillus* are the most common bacteria detected in soil incubated after irradiation (Peterson, 1962), the bacterial numbers observed probably result from the development of spore-forming bacteria and other microorganisms inadvertently introduced in the sample during the addition of Tc solution.

5. Soil respiration measurement

Soil respiration was recorded during the course of the experiment by CO_2 emission. At time intervals, entire samples were placed in closed vessels for 24 hrs. At the end of the 24 hrs incubation, the CO_2 evolved was quantified by gas chromatography (GC-8A Shimadzu with thermoconductivity detector - molecular sieve 5A and poropak Q columns).

Because the measurement of soil respiration was intended to verify that the reduction of microbial activity persisted for the duration of the experiment, the data on CO_2 evolution from the samples are presented and discussed in this section. Little CO_2 evolution was observed from the Bt samples. On the other hand, in spite of the drastic decrease in microbial numbers following the irradiation treatment (see above),

relatively elevated CO_2 levels were evolved from irradiated Ap samples (Fig. II.2).

High levels of CO_2 evolution from γ-irradiated soils have been observed by several authors (Powlson and Jenkinson, 1976; Peterson, 1962; Howard and Frankland, 1974; Powlson, 1975; Cawse and Mableson, 1971). It was shown that the phenomenon is partly due to the activity of enzymes located within "dead" bacterial cells. Following gamma radiation, there is no apparent alteration of the bacterial structure (Labeda et al., 1975) but the organisms are incapable of proliferation because of damages to their nucleic acids. Another possible source of CO_2 shortly after irradiation would be the radiolytic decarboxylation of organic matter.

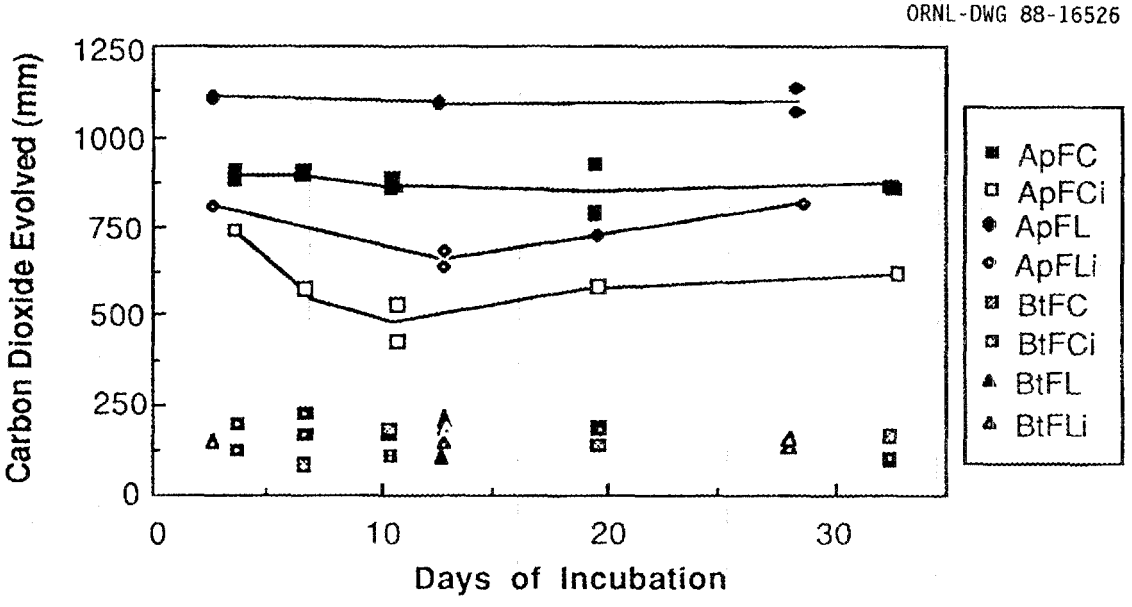

Fig. II.2. Carbon dioxide evolution from the samples during the course of the experiment. The Y axis gives a measure of the CO_2 evolved in 24 hrs (height of gas chromatography peak in mm).

Since the samples are no longer sterile at the end of the experiment, the CO_2 evolved from the irradiated Ap samples after a few weeks of incubation could be explained by the respiration of the developing microbial biomass.

These observations indicate that soil respiration in the irradiated samples is not a good indicator of soil microbial activity shortly after irradiation. Consequently, interpretation of the data for the irradiated samples is somewhat difficult. However, the data for the non-irradiated samples indicate (1) that no drastic change of the microbial activity took place during the course of the experiment since the soil respiration of ApFC and ApFL samples remained constant, and (2) that, as expected from the low microbial numbers, microbial activity in the Bt samples was negligible; the CO_2 present in the gas atmosphere was only slightly higher than the ambient CO_2 level.

6. Measure of sorption

The principle of the measure of Tc sorption is that the amount of TcO_4^- removed from the soil water is assumed to be sorbed. Soil water was collected from each sample by centrifugation. The sample was placed on a Wattman 40 paper filter (size 42.5 mm) into a centrifugation assembly (Fig. II.1.C, pp. 16) composed of a plastic buchner funnel with a 250 mL bottle screw cap fitted at the bottom. The assembly was spun in a swinging-buckets centrifuge at 2500 g for 30 minutes, and the water that percolated through the soil during centrifugation was collected from the bottom cap. The amount of soil water collected is dependent on the nature of the soil and its water tension. The technique allowed recovery of 33.3 $\pm$ 0.8% and 21.7 $\pm$ 1.41% of the total soil water for APFC&i and BTFC&i respectively.

The amount of Tc sorbed to the soil was calculated by the formula :

total Tc - {(Tc conc. in soil water) * total water},

based on the concentration of Tc in the collected soil water and the total amount of water (total water) and Tc (total Tc) in the sample prior to centrifugation. The underlying assumption of this calculation is that the non-sorbed Tc is evenly distributed in the soil water. This assumption is reasonable : when the sample was centrifuged for different amounts of time, the amount of water collected varied, but the Tc concentration remained unchanged.

7. Chemical form of Tc in the soil water

In order to differentiate between Tc present in the soil water as TcO_4^- or as Tc-complexed with soluble organics, soil water was collected from samples of all treatments incubated in the presence of Tc for a period of 30 days. A drop (10 μL) of the soil water was placed at the bottom of a thin layer chromatography (TLC) sheet precoated with alumina G and dried. The TLC sheet was placed in a tank containing a small amount of the solvent system (mixture of butanol : acetic acid : water in the ratio 4 : 1 : 5). After 3.5 hrs, the TLC sheet was dried, and the alumina gel was scraped in 8 sections. The pattern of migration of ^{95m}Tc in the soil water samples was compared to that of TcO_4^-.

8. Measure of the redox potential and the pH of the soil water

The redox potential and pH of 1 mL of the soil water contained in a spectrophotometry cuvette were measured immediately after centrifugation with a rod-shaped Pt electrode and a pH microelectrode (MI-710 combination pH probe, Microelectrodes Inc). The Ag/AgCl

reference electrode of the pH probe served as reference for the Pt electrode. Redox potentials were corrected to pH = 7 (Eh_7).

9. Technetium isotopes, analysis, and concentrations

Technetium-99 was added to the soil as sodium pertechnetate ($Na^{99}TcO_4$). In the samples destined for organic matter extraction, ^{99}Tc was traced with the gamma isotope ^{95m}Tc (as $Na^{95m}TcO_4$) in order to avoid the lengthy procedure necessary to prepare the soil organic matter extracts for beta counting (discoloration, volume reduction and removal of excess salts).

Technetium analysis on the soil water samples solely contaminated with the beta emitter was performed by liquid scintillation counting. On the organic matter extracts and soil water samples contaminated with the ^{95m}Tc isotope, Tc analysis was performed by gamma counting with a Germanium-Lithium detector accommodating large (150 mL) vessels.

The concentration of ^{99}Tc was 825 Bq (mL soil water) $^{-1}$ for the samples of all treatments used for the study of Tc sorption kinetics, and for the samples incubated at different water tensions. This concentration expressed in Bq (g soil oven-dry weight)$^{-1}$ varies with the kinetics treatments as shown in Table II.3, row B. Samples used to study the equilibrium distribution of Tc as a function of Tc concentration were submitted to 3 concentrations of Tc : 455, 825 and 1232 Bq (mL soil water)$^{-1}$ (rows A, B and C of Table II.3).

10. Determination of Tc equilibrium distribution as a function of soil water content and Tc concentration

Replicates of non-irradiated and irradiated samples were incubated for 15 days before sorption was measured. The incubation period of 15

days was chosen because kinetics studies (Ch. IV) indicated that an equilibrium distribution of Tc was reached in the sample within that amount of time.

The soil water contents, expressed in percent by weight [(soil water weight) x (dry soil weight)$^{-1}$x100] were : 22, 33 (field capacity), 43, 60, and 85 % (flooded condition) for Ap and 15, 24 (field capacity), 45, and 65 % (flooded condition) for Bt. The soil water Tc concentrations were : 455 (A), 825 (B), 1232 (C), and 2678 (D) Bq (mL soil water)$^{-1}$ (Table II.3).

Table II.3. Technetium added to each treatment

Treatment		Tc per mL[a] Soil Water (kBq (mL)$^{-1}$)	Tc per g Soil[b] (kBq (g oven-dry)$^{-1}$)
ApFC&i	A	0.45	0.15
	B	0.82	0.28
	C	1.23	0.42
	D	2.68	0.91
ApFL&i	A	0.45	0.39
	B	0.82	0.70
	C	1.23	1.05
BtFC&i	A	0.45	0.11
	B	0.82	0.20
	C	1.23	0.30
BtFL&i	A	0.45	0.30
	B	0.82	0.53
	C	1.23	0.80

a and b are equivalent expression of the amount of ^{99}Tc added to the samples.

11. Soil organic matter extraction procedure

After centrifugation to remove part of the soil water, a 15 g oven-dry equivalent of sample was taken for organic matter extraction. It was shaken for 1 hour in a 1:10 soil:solution ratio of 4 successive extractants, first an acid (0.075 M HCl), to remove the pertechnetate remaining in the soil water, then increasing NaOH concentrations in 0.05 M NH_4OAc ; 0.05 M (pH 9), 0.075 M (pH 10), 0.10 M (pH 11). The presence of ammonium acetate in the alkaline solutions enhances the solubility of the soil organic matter by complexing the Fe^{3+} ions that would otherwise be present on the functional groups and keep the humic matter coagulated.

After each extraction, the soil slurry was centrifuged in a swinging bucket centrifuge at 2500 g for 10 min. The extract was removed and the next extractant added without exposure to air by the positive pressure system described below (Fig. II.3). It is absolutely necessary to exclude oxygen from the samples during extraction in order to prevent a change in the species of Tc. Organic matter has a pronounced sensitivity to oxidation at high pH values (Swift and Posner, 1972). Alkaline autoxidation of the organic matter-Tc complexes and reoxidation of reduced forms of Tc would lead to a premature release of Tc in the first extracts upon exposure to air.

Description of the system used to avoid exposure of the soil organic matter extracts to air :

<u>Oxygen-poor solutions</u> : Sodium hydroxyde solutions were made by adding vigorously boiled water to a few milliliters of very concentrated NaOH solution and bubbling extensively with N_2.

<u>Removal of the extract from the centrifuge bottle</u> (Fig. II.3A) : The caps (a and b) of the centrifuge bottle were replaced by the rubber stopper I with a N_2 inlet and a long tubing. Nitrogen gas pressure was applied and the supernate was pushed into the collection bottle by positive

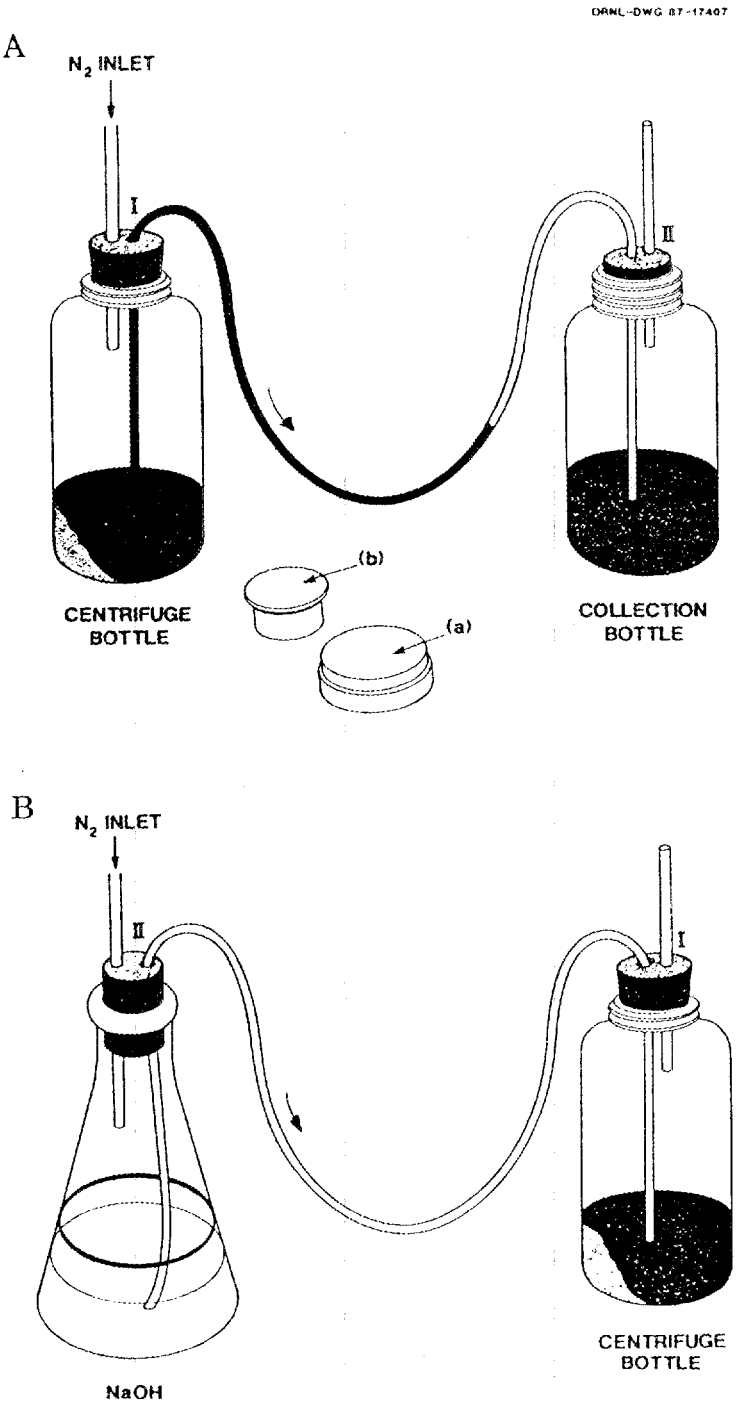

Fig. II.3. System used to avoid exposure of the soil organic matter extracts to air. (A) Removal of the extract from the centrifuge bottle. (a) cap lined with rubber, (b) screw cap. (B) Addition of NaOH solution to the soil pellet.

pressure. The N_2 inlet was moved to the rubber stopper II and the collection bottle was flushed with nitrogen.

Addition of the next extractant (Fig. II.3B) : The rubber stopper II was placed on the erlenmeyer containing a fresh NaOH solution and the alkaline solution was pushed into the centrifuge bottle. The N_2 inlet was moved back to the rubber stopper I to bubble N_2. The cap with rubber lining (b) and the screw cap (a) were placed back on the centrifuge bottle.

After removal of the 3 organic matter extracts, 36, 47, 21, and 19% of the total organic carbon remained in the soil residue of ApFC, ApFL, BtFC, and BtFL, respectively.

12. Characterization of the soil organic matter extracts

The organic matter fractions were characterized by their carboxylic acidity at pH 7, which was determined by precipitation with ^{60}Co-labelled cobalthexamine ($^{60}Co(NH_3)_6(NO_3)_2$), and their E4/E6 ratio. E4/E6 is the ratio of the optical density of the organic matter at 465 and 665 nm. It is mainly affected by the particle size of the humic material and its degree of condensation (Schnitzer and Khan, 1978), hence, it is indicative of the nature of the substance in solution. Humic acids are typically characterized by ratio values of 5 or less, whereas fulvic acids have a E4/E6 ratio of 6 or more (Schnitzer and Khan, 1978; Stevenson, 1982).

Precipitation with $^{60}Co(NH_3)_6(NO_3)_2$ (Stalmans, 1986) was preferred to the traditional methods for measuring organic matter acidity because the traditional methods require large amounts (50 to 100 mg) of purified organic matter whereas precipitation with cobalthexamine can be achieved using the entire soil organic matter extract. The method consists of adding an excess of ^{60}Co-labelled $Co(NH_3)_6(NO_3)_2$ complex to the soil organic matter extract. Rapid coagulation of the humic material takes place, enabling an easy phase separation by centrifugation. The

supernate is assayed for ^{60}Co, and organic matter acidity is calculated from the amount of ^{60}Co that disappeared from solution. The reproducibility of the method is reasonable down to 2 mg of organic matter.

Humic substances are polyfunctional; i.e. their reactive groups consist, in decreasing order of typical content, of carboxylic, phenolic, hydroxyl, quinone, amino and sulphydryl groups (Stevenson, 1982; Schnitzer and Khan, 1978). Since it was not clear which of these functional groups the cobalthexamine complex reacts with, the method was compared to standard methods to measure total acidity (barium hydroxyde method) and carboxylic acidity (calcium acetate). The total acidity and carboxylic acidity of 75 mg of a commercial purified humic acid (Aldrich Chemical Co.) were determined as described by Schnitzer (1982). For 5 replicates, the data obtained were 10.6 ± 1.3 and 4.8 ± 0.9 meq/g humic acid, respectively. Organic matter acidity, determined by cobalthexamine precipitation on 5 mg samples of the same humic acid, yielded a value of 5.3 ± 1.2 meq/g. This value is close to that obtained for carboxylic acidity. Therefore, it is likely that $Co(NH_3)_6(NO_3)_2$ reacts predominantly with the carboxylic groups, as Stalmans (1986) had suggested, and the method can be condidered as a measure of the carboxylic acidity of the organic matter at pH 7 (CA).

Carboxylic acidity (CA) measurements were performed in triplicate on soil organic matter extracts from 3 soil samples of each treatment by the following procedure : an aliquot of each extract was brought to pH 7 and mixed with an NH_4OAc (0.05 M, pH = 7) buffered solution of ^{60}Co-cobalthexamine. The mixture was centrifuged on a desk top centrifuge for 5 min, and the phases separated. The supernate was counted on a germanium-lithium gamma detector and the amount of coagulated cobalthexamine was calculated. To ensure that the functional groups of the organic matter were fully saturated, the operation was

repeated several times, with increasingly concentrated cobalthexamine solutions, until the amount of ^{60}Co precipitated remained constant.

The synthesis of $Co(NH_3)_6(NO_3)_2$ is documented in Bjerrum (1941). The synthesis of the ^{60}Co labelled compound is described below.

^{60}Cobalthexamine synthesis

Fifteen grams of $Co(NO_3)_2 .6 H_2O$ were dissolved in 30 mL of distilled water containing $^{60}CoCl_2$. Sixteen grams of NH_4NO_3, 0.8 g carbon, and 40 mL of 25% NH_4OH were added in the order mentioned. The mixture was stirred for 2 hrs with a powerful stream of air. Upon oxidation, the Cobathexamine salt precipitated. The precipitate was filtered and washed. To remove the carbon contaminating the precipitate, the cobalthexamine complex was re-dissolved in 1L of distilled water containing a little HNO_3. The solution was filtered from the carbon and precipitated with 120 mL of concentrated HNO_3. The mixture was left to cool and the liquid phase removed. The precipitate, a pure $^{60}Co(NH_3)_6(NO_3)_3$ salt of orange color, was washed successively with 60% and 90% ethanol, and dried at 100 ^oC.

13. Measure of the release of sorbed Tc upon drying

If Tc sorption occurs after its reduction to a lower oxidation state, then oxidizing conditions could promote its reoxidation to TcO_4^- and its subsequent desorption. Under natural conditions, a drastic oxidizing condition would be that of a dry soil.

Theoretically, the amount of sorbed Tc released upon drying could be calculated as the difference between the amount of Tc sorbed prior to drying and after drying. There is no experimental technique allowing direct measurement of the amount of sorbed Tc in the air-dried soil. Sorbed Tc is usually determined by soil:soil water partitioning of the total Tc present. However, if a large amount of water is added to the air-dried sample, Tc sorption proceeds rapidly (Fig. IV.2 pp. 51), the equilibrium

distribution of Tc in the soil is displaced towards sorption and is no longer representative of the air-dried condition. In the following experimental procedure, a minimum of water was added to the air-dried soil for a short period of time in order to minimize the risk of creating flooded conditions conducive to Tc sorption.

Soil samples contaminated with Tc were incubated for 15 days at the initial water tension (field capacity or flooded) then spread on a petri dish, air-dried and sieved through a USDA standard testing sieve # 10 with 2 mm openings. After 1, 5, 10, 15 and 90 days of exposure to air, the dry samples were poured in the centrifugation assemblies described above to collect soil water. Five milliliters of distilled water were added to them and they were spun for 30 min. at 2500 g. Typically, 2.29 $\pm$ 0.06 mL and 1.67 $\pm$ 0.19 mL water were recovered by centrifugation for Ap and Bt respectively.

The concentration of Tc in the recovered water was used to calculate the total amount of Tc in solution. Given the small amount of water passing through the soil and the short duration of the contact between the soil and the water, the total amount of Tc in solution (and, consequently, the amount of Tc desorbed) might be underestimated.

14. Drying /rewetting regime

Soil samples contaminated with Tc were incubated for 15 days at the initial water tension (field capacity or flooded) then spread on a petri dish, air-dried and sieved through a USDA standard testing sieve # 10 with 2 mm openings. After 10 days of exposure to air, they received distilled water to reach field capacity or flooded condition. The quantity of Tc sorbed was measured after 15 days of incubation under these new conditions.

CHAPTER III

BIOACCUMULATION AND CHEMICAL MODIFICATION OF TECHNETIUM BY SOIL BACTERIA

A. Introduction

Bacterial processes affecting radionuclides' mobility

The bacterial processes potentially affecting the mobility of radionuclides in the environment are numerous. Furthermore, since microorganisms are very resistant to ionizing radiation (Eriksen and Emborg, 1978), these processes can be expected to take place even in radioactive areas such as U tailings and radioactive waste disposal sites. Recently, problems of mobilization of radionuclides in low-level radioactive waste disposal sites have been related to microbial processes (Francis, 1985).

Some of the microbial processes acting to mobilize radionuclides are not directly related to the radionuclides and are specific to the disposal of low-level radioactive wastes in shallow-land trenches and pits. One of the problems encountered is the microbial decomposition of the waste material resulting in subsidence of the trench cover. In addition to the radionuclides, the bulk of the waste consists of organic material from nuclear power plants, hospitals, universities, radiopharmaceutical manufacturers, fuel fabrication industry, government energy research and military programs. Biodegradation of the organic waste leads to the settlement of the trench content and the subsidence of the trench cover. Water percolation into the trench is increased and the trench content overflows, contaminating surface land and groundwater (problem at the West valley facility, New York - Francis, 1985). Another problem is the

production of metabolic gases which result in container pressurization and explosion.

Other microbial processes indirectly affect radionuclide speciation and mobility. These processes are :

(1) Production of mobile water-soluble microbial metabolites or degradation products capable of forming stable water-soluble complexes with radionuclides that would otherwise be adsorbed on clay and soil particles. The solubilization of heavy metals by organic acids (Cole, 1979; Bloomfield and Pruden, 1975; Bolter et al., 1975; Knox and Jones, 1979) and the microbial production of Fe chelators (Cox and Graham, 1979; Leong and Neilands, 1976; Carrano and Raymond, 1978) are well known. Therefore, radionuclide complexation with polar organics of microbial origin is a likely mechanism for radionuclide migration away from disposal sites. Complexation of Pu by agents produced by microbial cultures has been demonstrated (Wildung and Garland, 1980), and Co, Sr, Cs and Pu have been found complexed with organic ligands in trench leachates (Cleveland and Rees, 1981; Kirby et al., 1982; Auerbach, 1974).

(2) Degradation of the organic species that keep radionuclides mobile (water-soluble chelators) or immobile (soil organic matter). Microbial degradation of strong chelators such as EDTA and NTA has been demonstrated (Tiedje, 1975; Tiedje and Masson, 1974).

(3) Change in redox potential and pH which affect the valence or ionic state of the radionuclides and modify their solubility characteristics. A microbially-mediated reduction of pH (for example, by oxidation of reduced S forms and production of SO_4^{2-}) increases the solubility of Cd, Pb, Ni, Cu, and Cr, whereas it decreases the solubility of Mo, Se, Sn, Ba, and As (Francis, 1985).

(4) Production of oxidants. For example, Fe-oxidizing bacteria produce ferric ions that oxidize UO_2 (insoluble) to UO_2^{2+} (soluble). This process is exploited on a commercial scale for extraction of U from ores.

(5) Production of hydrogen sulfide that forms sulfides of low solubility with metals.

Other processes involve the metabolism of the radionuclides by bacteria :

(1) Production of radioactive gases like $^{14}CO_2$, $^{14}CH_4$, CH_3T, $^{14}CH_3T$, HTO, T_2, and HT. Tritiated methane is one of the most abundant gaseous compounds released from various waste disposal trenches (Matuszek, 1980)

(2) Direct oxidation of the radionuclide. It has been demonstrated that in the absence of Fe, UO_2 is oxidized directly to UO_2^{2+} by *Thiobacillus ferrooxidans* (Tuovinen and DiSpirito, 1984).

(3) Radionuclide bioaccumulation. Microbial bioaccumulation of Sr, U, Co, I, Cs, Ra, Th, Am, and Pu has been observed (Strandberg et al., 1981 (a,b), Shumate et al., 1978, Tsezos and Volesky, 1981; Giesy and Paine, 1977; Beckert and Au, 1976, Strack and Müller, 1984), and the use of microorganisms in radionuclide removal from waste process streams has been suggested (Shumate et al., 1978; Strandberg et al., 1981b; Brown and Lester, 1979). Accumulation in the bacterial biomass not only immobilizes radionuclides, but also modifies their transport properties; radionuclides migrate to the ground water with the bacteria and are released upon cell lysis.

Changes in chemical speciation may have drastic consequences on radionuclide mobility and plant availability and, therefore, alter radionuclide food chain transfer and the potential exposure of human populations. In recent years, the importance of microbial transformations of radionuclides for risk assessment has been recognized (Bonnyns-Van Gelder and Kirchmann, 1984) but there is still little known of the processes and their environmental significance.

In the case of Tc, there is evidence for the involvement of microbial activity in Tc sorption in soil; Tc sorption is decreased at low temperature (Mousny and Myttenaere, 1981) and after autoclaving (Landa et al., 1977),

and is enhanced with glucose addition to the soil (Van Loon et al., 1986b). However, the extent of bacterial involvement and the mechanisms for the microbial effect are unknown.

Both direct and indirect mechanisms could explain the role of microbial metabolism on Tc sorption. The potential *direct* mechanisms are : a) bioaccumulation in the bacterial biomass, b) uptake and excretion as a modified, less mobile form (valence state lower than VII or Tc associated with organic molecules). Pertechnetate could also be affected *indirectly* by a) physico-chemical modifications of the local environment (redox potential and pH) leading to a reduction of TcO_4^-, or b) production of metabolites able to complex and/or reduce TcO_4^-.

Microbial polysaccharides (capsule polysaccharides [CPS] and exopolysaccharides [EPS]) are metabolites that could potentially complex Tc. Indeed, Tc complexes with polysaccharides such as starch have been synthesized under strongly reducing conditions (Paquette et al., 1980), and CPS and EPS are known for their binding potential with metal ions (Tan and Loutit, 1976; Mittelman and Geesey, 1985; Martin et al., 1975; Brown and Lester, 1979).

The involvement of bacteria in the oxidation and reduction of elements presenting several valence states is common. Nitrogen, Fe, Mn, and S are well known elements for which oxidation and reduction are microbially-mediated processes. Several factors (competition for plant uptake, Tc association with sulfur aminoacids) suggest that TcO_4^- could be a analog of sulfate in biochemical processes. Sulfate-reducing bacteria reduce S from the valence +VI (SO_4^{2-}) to -II (H_2S). It seemed valuable to investigate if these bacteria could also reduce Tc from the state +VII (TcO_4^-) to +IV (TcO_2).

Objectives

The objectives of this study were (1) to identify the mechanisms by which bacteria could affect the solubility of Tc in soil, (2) to investigate a specific role of sulfate-reducing bacteria in the biomodification of TcO_4^-, and (3) to determine if bacterial polysaccharides bind Tc.

With respect to objective (1), immobilization of Tc in soil microbial biomass has been referred to as a possible mechanism for long term retention of Tc in soil (Van Loon et al., 1986b; Pignolet et al., 1986). This hypothesis is discussed in light of the observed bioaccumulation of TcO_4^- by mixed cultures of both aerobic and anaerobic soil bacteria.

B. Results

1. Bioaccumulation

Mixed aerobic bacteria

The mixed cultures of aerobic bacteria did not substantially accumulate Tc. Over a 40 hour period, the highest bioaccumulation value (CR) recorded was less than 15 (Fig. III.1A). It corresponded to a vigorously growing population (Fig. III.1A), and a drop in pH and redox potential (Fig.III.1B). In cultures grown for longer periods of time, slightly higher CR values were observed, but none of 5 predominant strains isolated from these "older" cultures showed an extraordinarily high CR value (Table III.1). The CR values obtained for the mixed cultures (Fig. III.1A and Table III.1) and the isolates (Table III.1) ranged from 3 to 28.

Mixed anaerobic bacteria

The accumulation of Tc in anaerobic bacteria was much higher than in aerobic bacteria (Fig. III.2A). The CR values observed over a 200 hour period ranged from 50 to 600. The fluctuation of the CR values with

Table III.1. Bioaccumulation (CR) of Tc in mixed cultures and pure cultures (isolates) of aerobic bacteria.

ORGANISMS	DURATION OF GROWTH IN PRESENCE OF TC (h)	TC CONCENTRATION IN MEDIUM (Bq L^{-1})	CR[a]
mixed culture	140	621	27
mixed culture	140	621	24
mixed culture	70	62.1	18
mixed culture[b]	70	62.1	21
mixed culture[b]	70	62.1	28
isolate 1 [c]	70	62.1	25
isolate 2 [c]	70	62.1	21
isolate 3 [c]	70	62.1	18
isolate 4 [c]	70	62.1	11
isolate 5 [c]	70	62.1	7

a. CR = concentration ratio [dpm Tc (g bacteria dry weight)$^{-1}$ divided by dpm Tc mL^{-1} medium]

b. in these cultures, the bacteria were grown for 7 days before the addition of pertechnetate.

c. the isolates were obtained from a 70 hrs old mixed culture.

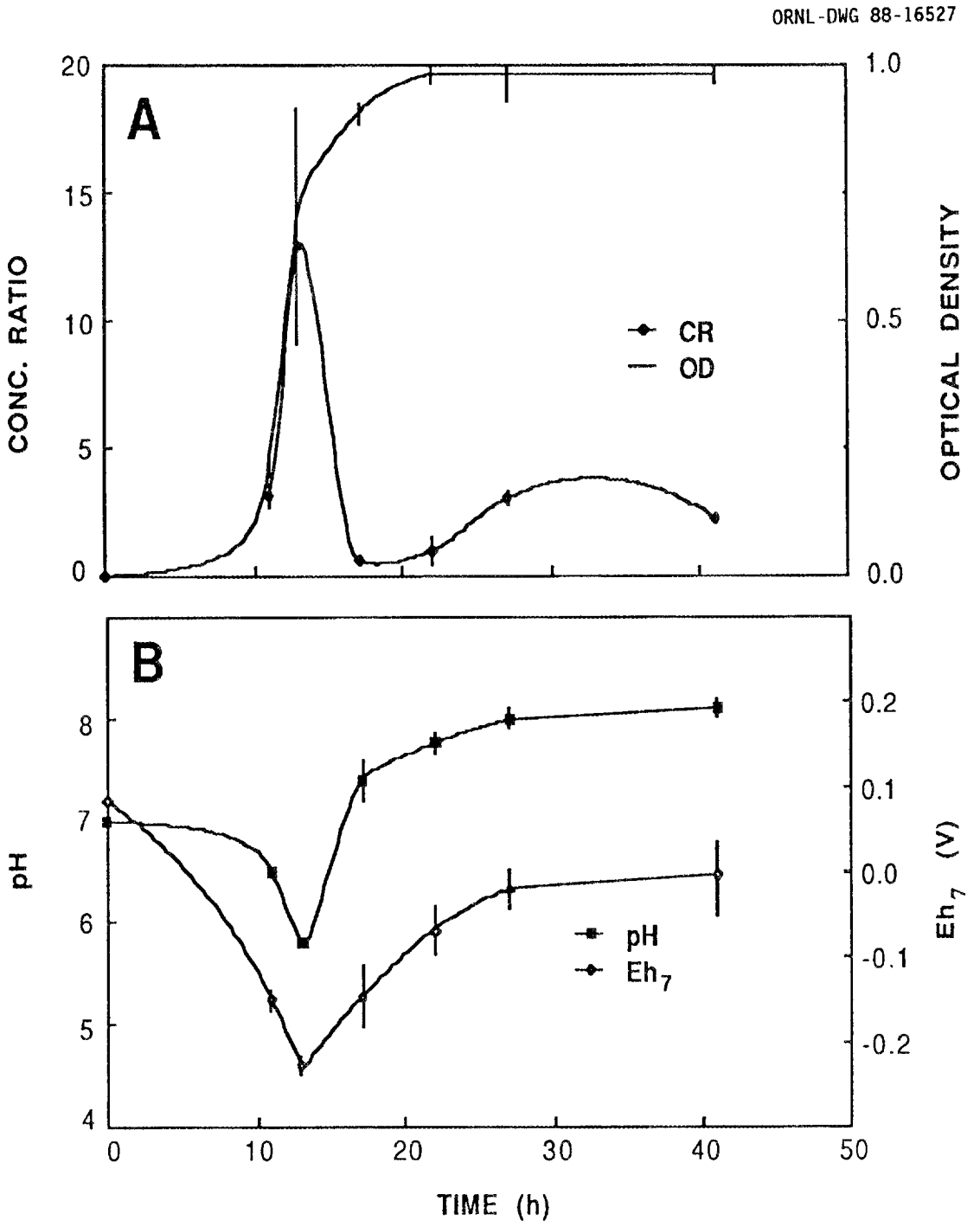

Fig. III.1. Mixed aerobic bacteria. (A) : Growth and bioaccumulation of pertechnetate as a function of time. (B) : Eh and pH changes during growth. The mean and standard error of 4 replicates are represented for each measurement.

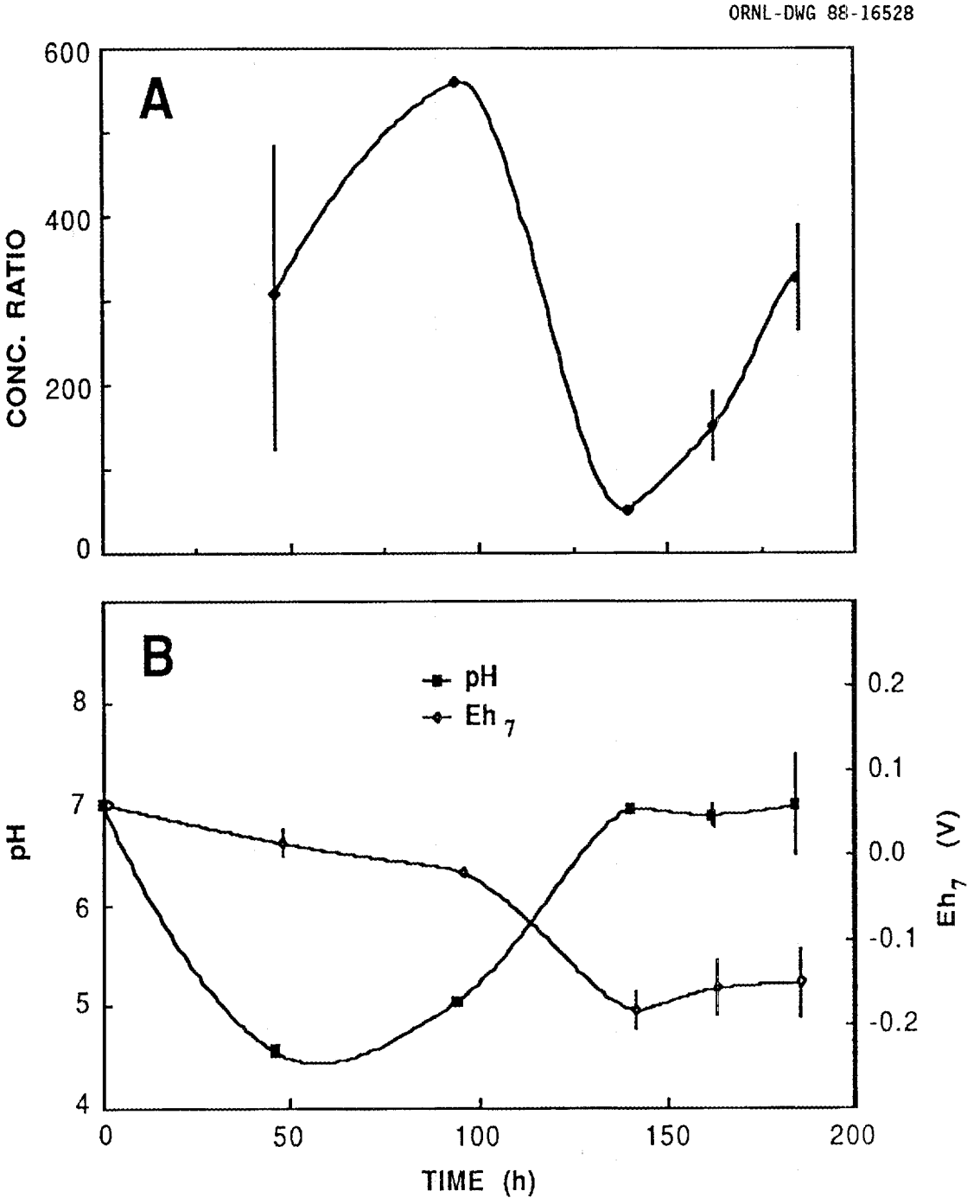

Fig. III.2. Mixed anaerobic bacteria. (A) : Bioaccumulation of pertechnetate as a function of time. (B) : Eh and pH evolution during growth. The mean and standard error of 4 replicates are represented for each measurement.

time was probably due to the succession of different sets of strains, as the trend of pH and Eh in Figure III.2B suggests.

Sulfate-reducing bacteria

As much as 70% of the total Tc in the culture was associated with the pellet of sulfate-reducing bacteria. Expressed as bioaccumulation, these very high amounts of Tc gave rise to extremely elevated CR values (Table III.2).

Table III.2. Amounts of Tc associated with the sulfate reducing bacteria expressed in terms of concentration ratio (mean and standard error of 4 replicates).

ORGANISM	CR
D. vulgaris	9311 ± 3710
D. gigas	6974 ± 2832

2. Chemical form of Tc in the growth medium

Mixed aerobic bacteria

Technetium in the aerobic medium always eluted from the Biogel P2 chromatography column in a single peak corresponding to pertechnetate (Fig. III.3A).

Mixed anaerobic bacteria

A fraction of the technetium in the growth medium was associated with soluble organics. This non-pertechnetate fraction increased with time. Figure III.3B shows the distribution of technetium in the medium after 162 hours in the presence of the bacteria (16.5% of the Tc was present as non-pertechnetate). When pertechnetate was equilibrated with the growth medium after removal of the bacteria, the association with the

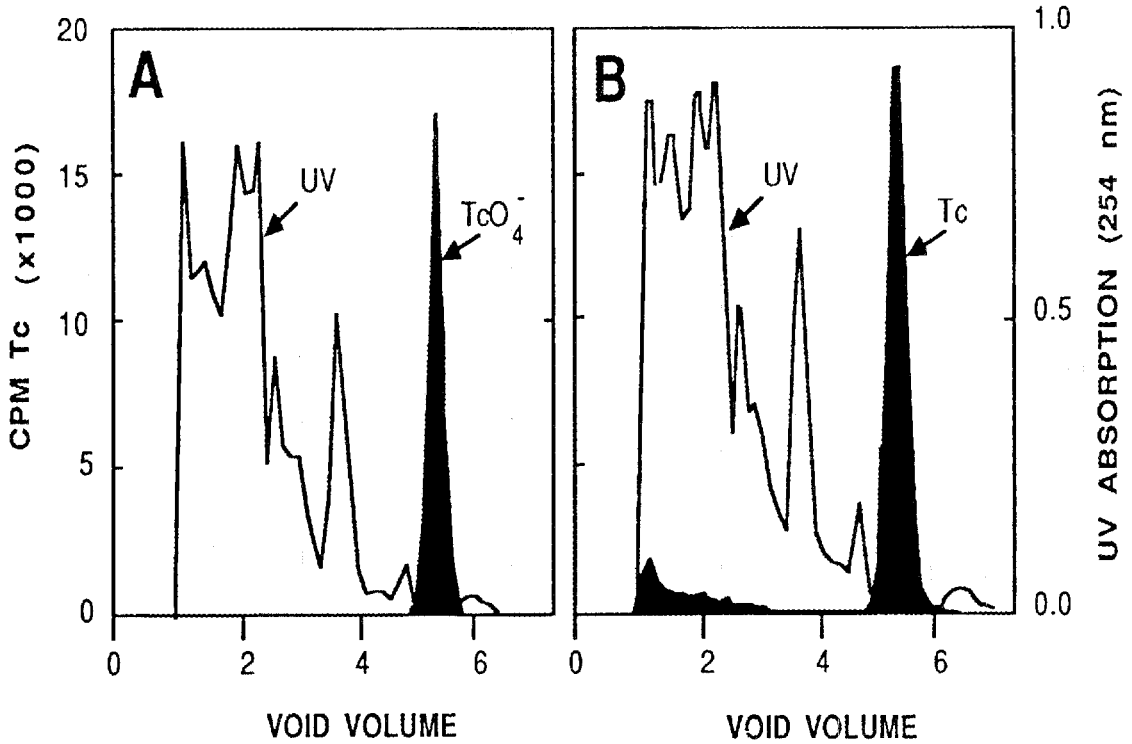

Fig. III.3. Chemical form of Tc in the growth medium of (A) mixed aerobic bacteria, and (B) mixed anaerobic bacteria after 162 hours of growth.

organics did not take place and freshly added Tc eluted as pertechnetate. This suggests that the association of Tc with the organics is the result of a *direct* action of the mixed anaerobic bacteria on pertechnetate.

Sulfate-reducing bacteria

All the Tc in solution was associated with organics in the growth medium of these bacteria (Fig. III.4A). This distribution was similar to these obtained when (1) pertechnetate and a strong reductant (sodium dithionite, final concentration 3 mM) were added to the medium in the absence of bacteria, or (2) when pertechnetate was added to the growth medium after removal of the bacteria (Fig. III.4B). Unlike in the case of

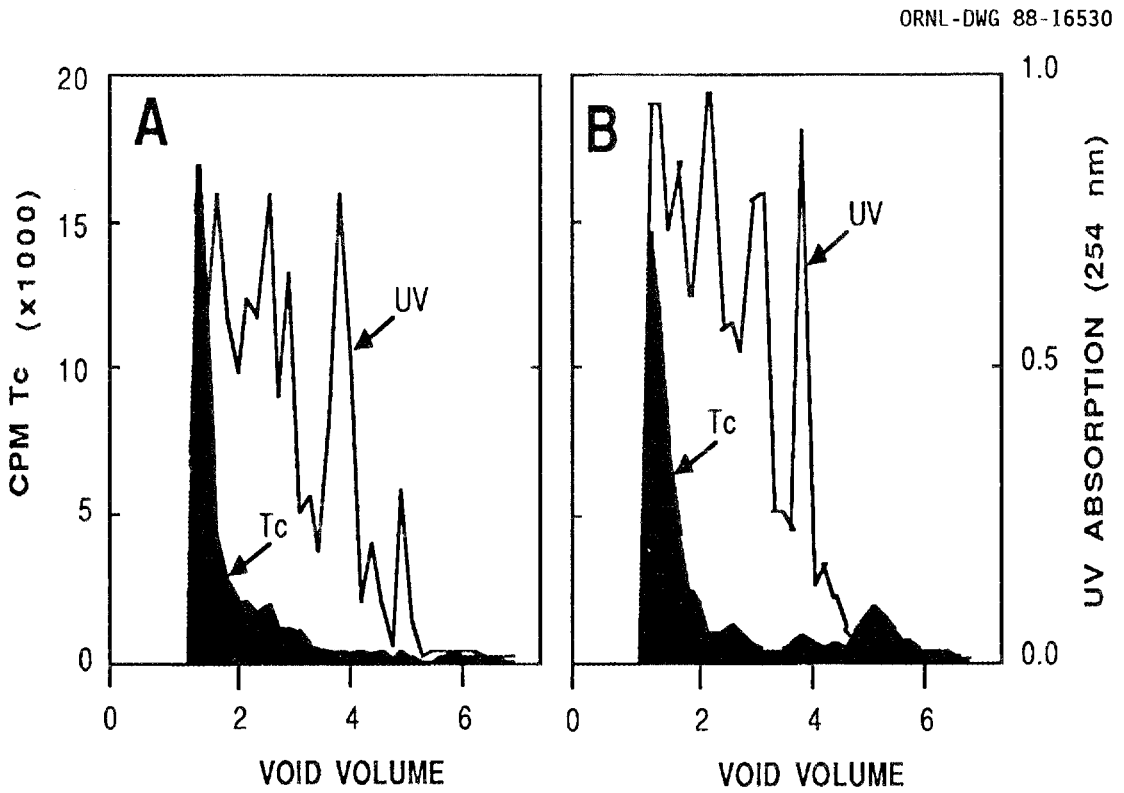

Fig. III.4. Chemical form of Tc in the growth medium of sulfate-reducing bacteria : (A) in the presence of sulfate-reducers, and (B) with pertechnetate added after growth and removal of the bacteria.

the mixed anaerobic bacteria, the association of Tc with organics appears, here, to be an *indirect* effect of the sulfate-reducing bacteria's metabolism, and in particular the result of a reducing agent's presence in the growth medium.

3. Association of Tc with the CPS and EPS fractions

In mixed aerobic bacterial cultures, no Tc was found in the CPS fraction. In mixed anaerobic bacterial cultures, a small amount of Tc was associated with the CPS fraction (8.2 $\pm$ 4.2 % of the total Tc in the bacterial pellet; 4 replicates), and with the EPS fraction (2.4 $\pm$ 2.1 % of the total Tc in the growth medium; 4 replicates).

C. Discussion

Aerobic bacteria had *no* apparent effect on TcO_4^- : there was little bioaccumulation and no evidence for the modification of the chemical form of Tc. However, even in well-aerated soil there is evidence for a microbially-mediated sorption of pertechnetate (see Chapter IV). Consequently, sorption under these conditions must be related to the activity of anaerobic or facultative aerobic bacteria in soil microsites where the diffusion of oxygen is poor and the redox potential low.

Tc immobilization in the soil microbial biomass

Incorporation into microbial biomass has been invoked as a mechanism to explain the retention of Tc in soil (Van Loon, 1986b; Pignolet et al. 1986). In the present experiments, only anaerobic bacteria accumulated Tc. Assuming that all bacteria of the soil accumulated Tc with a CR typical of that observed for anaerobic bacteria, the fraction of Tc that would be accumulated in the soil microbial biomass in one turnover time was calculated.

Considering that a typical soil contains from 10^8 to 10^9 bacteria per gram of soil, and that the average weight of a cell is 1.5×10^{-5} μg, the total live weight of bacteria would range from 0.15 to 1.5 mg(g soil)$^{-1}$ (Stevenson, 1982). However, only 10 to 40% of the total biomass is believed to be active at one given time (Paul and Voroney, 1984; Clarholm and Rosswall, 1980), such that the biomass of active bacteria in 1 g of soil would be 0.06 to 0.6 mg. If one assumes (1) that all of the bacteria of the soil accumulate Tc with a CR of 600 (150 on a fresh weight basis), and (2) that the concentration of ^{99}Tc in the soil solution is 621 BqL^{-1} (concentration used to determine the experimental CR), the amount of Tc accumulated in the bacteria [given by concentration x CR [fresh weight basis] x active bacterial biomass] would be 5.58 to 55.8 mBq. In other words, in 1g of soil in equilibrium with 1 ml of soil solution containing

621 mBq, under the above assumptions, 0.9 to 9.0 % of the Tc would be associated with the bacterial biomass in one turnover time. In general, turnover times of microbial biomass in soil are long, 3 to 4 orders of magnitude greater than those of organisms growing under optimal laboratory conditions (Jenkinson and Ladd, 1981; Clarholm and Rosswall, 1980; Shields et al., 1973). (Turnover times can however be locally increased, for example, in the rhizosphere.)

In conclusion, given the total microbial biomass and the generally long turnover time of the bacteria in soil, bioaccumulation does not seem a likely mechanism for long term retention of Tc in soil, even though some observed CR values are high. The variation of CR as a function of Tc concentration has not been considered here, and could possibly modify the results of the calculation performed above. The distribution of Tc among the bacterial components *and* the residence time of these components in soil would also ultimately determine the long term effect of Tc accumulation by bacteria.

Modification of Tc chemical form by anaerobic bacteria

Technetium associates with organics only in its reduced form (valence state lower than that of TcO_4^-) (Carlsen et al., 1984). Van Loon and coworkers (1986b) showed that a facultative anaerobe (*E. coli*) grown anaerobically in the presence of an organic matter extract promoted the formation of Tc-organic matter complexes over time. The data presented here suggest that the mixed anaerobic bacteria directly reduced TcO_4^- rather than merely created the environmental conditions necessary for its reduction and complexation. A likely mechanism for the reduction of TcO_4^- to a lower valence state would be that, in the absence of oxygen, the TcO_4^- ion is used by the bacteria as an electron acceptor in anaerobic respiration, as in the case of nitrate, and ferric and manganic oxides. This hypothesis is supported by the existence of a large variety of bacterial

reductases and the similarity of standard redox potential between the TcO_4^-/TcO_2 half-reaction and the half-reactions of other redox couples used by bacteria.

The organisms performing nitrate reduction and the nitrate reductases they contain are diverse (Payne, 1981; Knowles, 1982). Furthermore, denitrifying bacteria also frequently possess reductases that allow them to use MnO_2 and $Fe(OH)_3$ as terminal electron acceptors as well (Lovley et al., 1987; Lovley and Phillips, 1986; Burdige and Nealson, 1985; de Vrind et al., 1986; Bromfield and Davis, 1976; Ghiorse and Ehrlich, 1976; Sørensen, 1982). Based on the high diversity of reductases and the versatility of the organisms, reduction of TcO_4^- by a nitrate, ferric- or manganic- oxide reductase is plausible. The standard potential of the TcO_4^-/TcO_2 half-reaction is 738 mV, close to those of NO_3^-/NO_2^- (835 mV), MnO_2/Mn^{2+} (1229mV) and $Fe(OH)_3/Fe^{2+}$ (1057 mV) (Bard et al., 1985; Glinski and Stepniewski, 1985). Pertechnetate could therefore be used as a terminal electron acceptor in the bacterial respiratory chain with a gain of energy comparable to the gain when nitrate, manganic- and ferric oxides are terminal acceptors.

Association of Tc with CPS and EPS was observed only in the cultures of anaerobic bacteria, further suggesting a role of these bacteria in Tc reduction and complexation with organics. However, the experimental variability in the quantity of Tc associated with CPS and EPS was too large to allow definitive conclusions concerning the affinity of Tc for these chemicals, and an eventual role of microbial polysaccharides in the immobilization of Tc in soil.

Since the bacterial cultures accumulated Tc only when they were grown in anaerobiosis, Tc bioaccumulation could be related to the direct reduction of TcO_4^-. High concentration factors for Tc in a marine *Planococcus* were also observed only when the organisms were grown under limiting oxygen tension (Pignolet et al., 1986).

Sulfate-reducing bacteria

The concentration ratios observed for sulfate-reducing bacteria appear too high to be derived solely from a biological process. Since the bacteria produce hydrogen sulfide which can react with TcO_4^- to form insoluble Tc sulfides (TcS_2, Tc_2S_7) (Paquette et al., 1980), the Tc associated with the bacterial pellet could be due to Tc accumulated in the bacterial cell or to the presence of inorganic precipitates. However, attempts to separate bacteria from the hypothetical precipitates by centrifugation on a sucrose gradient failed. This possibly resulted from an inadequate technique or from binding of the insoluble compounds to the bacterial surface. Regardless of the origin of the high amount of Tc associated with the bacterial pellet, it is clear that sulfate-reducing bacteria are extremely efficient in removing Tc from solution. They are likely to have a significant impact on the fate of Tc in environments where their population is large, e.g. in sediments and flooded soils.

The association of Tc with organics of the growth medium of sulfate-reducing bacteria indicates that TcO_4^- was reduced. Technetium reduction seems however to be the result of the release of a reducing agent in the growth medium rather than a direct reduction by the sulfate-reducing bacteria. Indeed, Tc association with the organics also occurred in the growth medium after removal of the bacteria. Furthermore, metabolism of TcO_4^- by the same mechanism as dissimilatory sulfate reduction seems unlikely. Sulfate is reduced to sulfide in a sequence of 3 reactions involving specific enzymatic complexes. The first reaction (activation of SO_4^{2-} by ATP) is inhibited only by analogs of SO_4^{2-} with 2 negative charges. These analogs form stable activation products with ATP (Postgate, 1984). This specificity suggests that analogs with 1 negative charge do not comply with the steric requirements of the enzymatic complex.

CHAPTER IV

SORPTION AND DESORPTION OF TECHNETIUM IN SOIL

A. Introduction : Behavior of Tc in Soil

The behavior of Tc in soil is important for the biogeochemical cycle of Tc because it will determine potential for Tc movement and plant availability. Technetium sorption to soil has been extensively studied; however, the results are confusing. The observation that little Tc is retained by soils in laboratory experiments conflicts with the low extractability and the decrease in bioavailability of Tc observed in field and lysimeters studies. Desorption of Tc from soil has received little attention. It is, however, a potentially important parameter for the long-term behavior of Tc. If sorption is important and non-reversible, then, contrary to the previous belief of its high geomobility, Tc can be considered as a poorly mobile element over the long term. If desorption is highly and rapidly reversible, the potential for high Tc mobility and plant uptake will be maintained. An adequate description of Tc behavior in soil, therefore, requires a knowledge of the kinetics and extent of the sorption and desorption processes, and of the environmental factors affecting both.

Factors affecting Tc sorption

Weak Tc sorption under laboratory conditions has been related to the organic matter content, the pH, the Fe content, the temperature, and the microbial activity of the soils studied.

In a number of studies (Sheppard et al., 1983; Landa et al., 1977; Mousny and Myttenaere, 1981), Tc sorption has been positively correlated with soil organic matter content, suggesting an association of Tc with humic material. Complexation of Tc with soil organic matter under strongly reducing conditions (Van Loon et al., 1986b) and the partial

recovery of sorbed Tc by weak alkaline solution (Landa et al., 1977; Bondietti and Garten, 1986; Garten et al., 1984; Garten et al., 1986) further implicated organic matter as a possible sink for sorbed Tc.

The effect of pH on Tc sorption is difficult to differentiate from that of soil organic matter since low pH and high organic matter are often concomitant. It could also be related to positive charges developed on amorphous Fe and Al oxides at low pH, which make the latter susceptible to capture anionic species. Wildung and coworkers (1986) reported that low sorption observed on forest-marshland soils was positively correlated to their extractable Fe and organic matter content. The correlation between sorption and extractable Fe content was stronger in the first 48 hours of the experiment. The authors suggested the sorption of Tc on the pH-dependent sites of the Fe and Al oxides.

A role of the microbial flora in the sorption process is suggested by an increase in sorption with the addition of glucose (Van Loon et al., 1986b), and by a decrease in sorption at low temperature (Mousny and Myttenaere, 1981) and after autoclaving (Landa et al., 1977). With the addition of growth medium and *E. coli* inoculum, high Tc sorption was obtained within 1 week (Van Loon et al., 1986b). The extent of microbial involvement in Tc sorption under field conditions, however, remains speculative. Addition of rapidly assimilable organics drastically increases the soil microbial biomass, making it an overriding factor when, in fact, its role could be small. Low temperatures reduce microbial activity but also chemical reaction kinetics. Autoclaving severely modifies the organic matter, and thus alters the likely sites for Tc retention.

The effect of redox conditions on Tc behavior in soil has not been studied systematically. However, the chemical properties of Tc and the strong sorption observed in anoxic sediments (Pignolet et al., 1986) or in soils maintained in anaerobiosis (Landa et al., 1977), indicate that the redox state of the soil is likely to significantly affect Tc sorption.

Discrepancy between laboratory and field observations

The quantity of Tc sorbed, and the kinetics of the process, differ widely among laboratory studies and conflict with the observed behavior of Tc under field conditions. Typically, sorption observed in the laboratory under aerated conditions is low (Wildung et al., 1986; Routson et al., 1977; Balogh and Grigal, 1980; Sheppard et al., 1983). In field and lysimeter studies, however, Tc becomes non-extractable and unavailable for plant uptake with time (Garten et al., 1984; Hoffman et al., 1982a,b; Sheppard and Sheppard, 1986; Vandecasteele et al., 1986).

This discrepancy is partly due to differences in soil properties, but also stems from the techniques used to assess the potential for soils to sorb Tc. The approaches taken to describe Tc sorption in soil have been : (1) air-dried soil shaken with an equilibrating Tc solution in closed vessels (Routson et al., 1977; Landa et al., 1977), in open vessels bubbled with oxygen (Gast et al., 1978), or agitated (Wildung et al., 1986; Sheppard et al., 1983); and (2) Tc solution added on a column of air-dried soil (Balogh and Grigal, 1980; Mousny and Myttenaere, 1981). Different techniques applied to the same soils can yield opposite conclusions regarding Tc sorption; for example, soil slurries incubated in closed vessels for 2 to 5 weeks sorbed 99% of the Tc in solution (Landa et al., 1977) whereas Tc passed unsorbed through columns of the same air-dried soils (Balogh and Grigal, 1980).

The shortcomings of these techniques are that they alter considerably the soil parameters likely to govern Tc sorption in the field. Air-drying the soil drastically affects its microbial population (Sparling and Cheshire, 1979, Bartlett and James, 1980). A soil slurry contained in a closed vessel promotes reducing conditions and, likely, Tc sorption. A well-aerated soil slurry is not equivalent to a well-aerated soil because the soil structure is destroyed. In a structured soil, inside the soil aggregates, oxygen diffusion is low and anaerobic bacteria flourish (Skinner, 1975; Wakao and Furusaka, 1976). In a soil slurry, these anaerobic microsites are absent. In light of the role of anaerobic bacteria

in the reduction process of Tc (Chapter III), the absence of these anaerobic microsites could affect Tc behavior. Another factor responsible for the discrepancy between laboratory and field results is the equilibration time between Tc and soil; many of the laboratory experiments were conducted for only a short period of time (e.g. 24 hrs).

On the other hand, under lysimeter and field conditions, Tc disappearance from the liquid phase can result from various simultaneous processes such as downward movement, uptake by vegetation, and sorption to soil. It is therefore difficult to determine the relative contribution of soil sorption to the overall disappearance of Tc.

There is a need to develop a methodology that would assess the contribution of soil sorption to the decrease in bioavailability, by providing data on the sorption of Tc under conditions of soil:water ratios and microbial activity realistic for the field.

Desorption of Tc from soil

Little data is available from the literature concerning the release of sorbed Tc from soil and none is available on the behavior of Tc under fluctuating water tension. Bondietti and Garten (1986) observed a release of 20% of the Tc sorbed following equilibration of the soil with an anion-exchange resin. The rate of Tc release under these conditions was determined as 0.015 $days^{-1}$. Stalmans (1986) observed that suspensions of Tc-soil organic matter complexes released Tc under oxygen flux. The reoxidation rate of the Tc complexes was a function of the nature of the organic material.

Objectives

The objectives of this work are :

(1) to provide data on the kinetics and the extent of Tc sorption and desorption in soil under soil:water ratios and microbial activity realistic for the field,

(2) to determine the importance of certain parameters in governing Tc sorption in soil, in particular microbial activity, soil water content, organic matter, and Tc concentration, and

(3) to describe the behavior of Tc in soil under fluctuating water tension.

Two horizons of an Ultisol were used in the study to contrast Tc behavior in a soil containing organic matter and supporting a high microbial activity (Ap horizon) and in a soil poor in organic matter and supporting a low bacterial population (Bt horizon).

B. Results and Discussion

1. Sorption kinetics and equilibrium distribution of Tc in soil : Effect of soil type, microbial activity, and soil water content

Figures IV.1 and IV.2 contain information on the kinetics of sorption and on the equilibrium distribution of Tc in soil as affected by the soil type (top soil: Ap and sub soil : Bt), the microbial activity (soil non-irradiated and soil γ-irradiated), and the soil water tension (field capacity (FC) and flooded (FL) conditions).

In the top soil at field capacity (ApFC, Fig. IV.1), sorption was initially rapid. As the amount of Tc sorbed increased, sorption slowed and reached a near-equilibrium value 15 days after introduction of TcO_4^-. At equilibrium, about 50% of the Tc initially present had been sorbed. A reduction of the microbial activity substantially affected both the kinetics and the equilibrium state of the process (ApFCi, Fig. IV.1).

In the sub soil at field capacity, a low sorption equilibrium value was rapidly obtained (BtFC, BtFCi, Fig. IV.1), and no difference in sorption behavior between the non-irradiated and the γ irradiated soil could be observed.

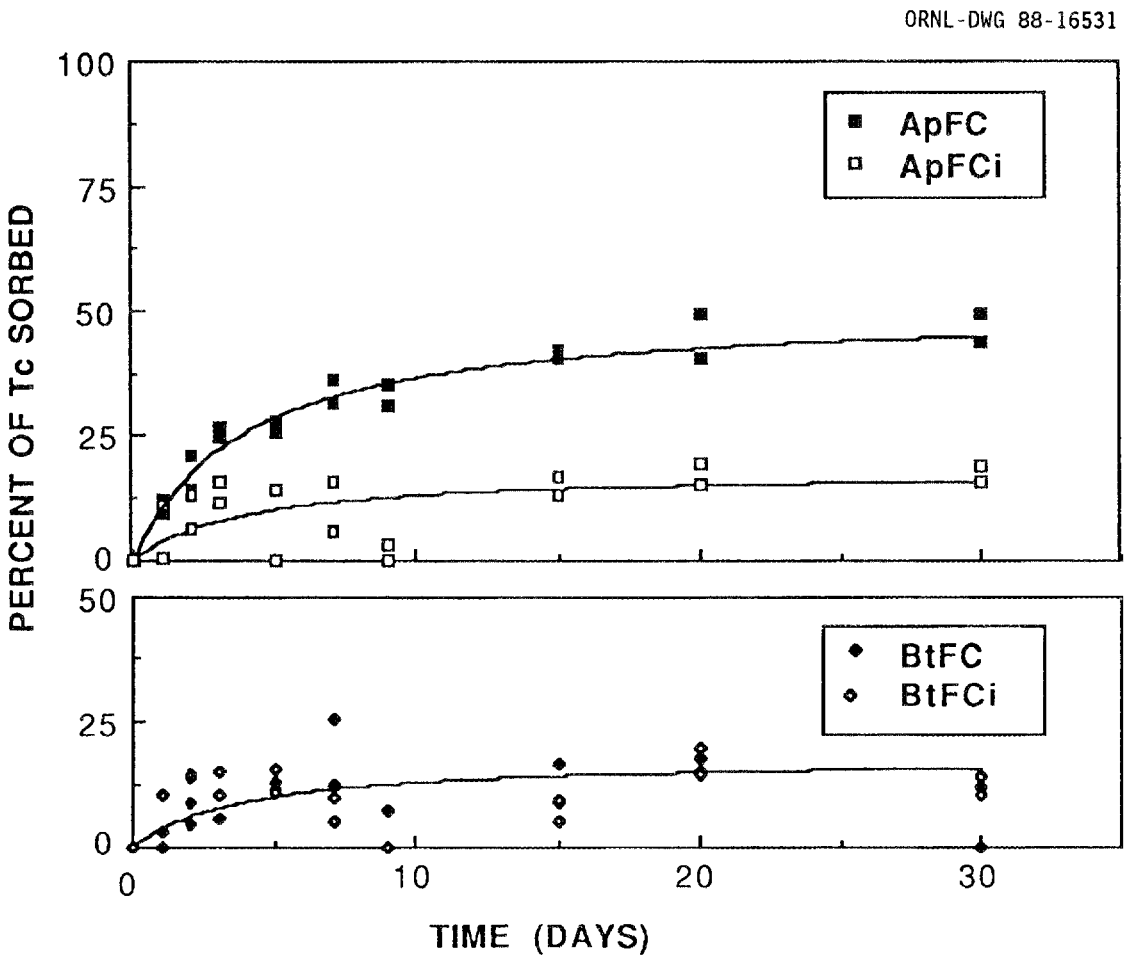

Fig. IV.1. Sorption of Technetium in soils incubated at field capacity.

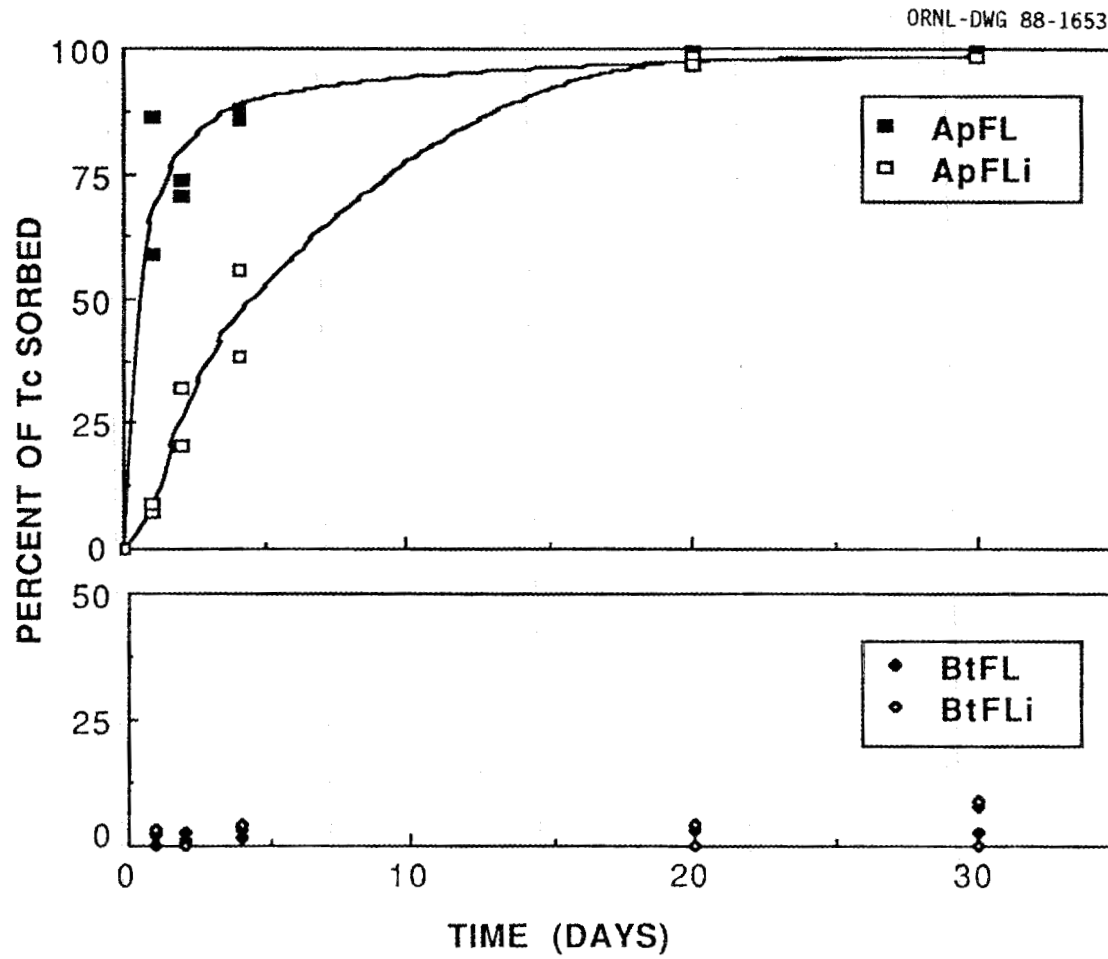

Fig. IV.2. Sorption of Technetium in soils incubated under flooded conditions.

In the topsoil under flooded conditions (ApFL, Fig. IV.2), Tc sorption was extremely rapid compared to that of ApFC. Complete disappearance of Tc from the soil water occurred within a few days.

Reduction of microbial activity delayed the process (ApFLi, Fig. IV.2), but complete sorption was nevertheless reached after 20 days of incubation. The sorption observed in the irradiated soil could be the result of a slow kinetics of reduction by abiotic processes since the prevalent conditions are reducing (Fig. IV.3), or more likely, the result of a re-growth of bacteria in the samples, leading to a progressive sorption as the microbial population increased. Indeed, the bacterial numbers in ApFLi increased from $3x10^2$ after irradiation to $8x10^6$ after 30 days of incubation (see discussion in Chapter II, pp.18).

In the subsoil under flooded conditions (BtFL,BtFLi, Fig. IV.2), the percentage of Tc sorbed was close to zero. The difference in percentage of Tc sorbed between BtFC and BtFL was probably due to the fact that the total amount of Tc in the BtFL samples is much larger than in the BtFC samples. (The initial Tc concentration in the soil water is the same for both treatments but the amount of soil water is larger in the case of BtFL.) In fact, the quantity of Tc sorbed in the 2 treatments was fairly similar.

In conclusion, the soil type is the main factor determining the extent of Tc sorption. The top soil, containing organic matter (2.73%) and supporting a high microbial population ($2x10^{10}$ bacteria per gram of soil), had a high retention capacity for Tc . In contrast, the subsoil, which has a low organic matter content (0.51%) and a low bacterial count ($2x10^5$), sorbed little Tc. In the top soil, soil water content and microbial activity had a large effect on the sorption process.

In field studies, it was shown that top soils have a high potential for Tc sorption. Indeed, Garten et al. (1984), Hoffman et al. (1982a,b), and Sheppard and Sheppard (1986) observed that most of the Tc applied on the soil surface remained in the upper few centimeters of the soil profile. In contrast, no sorption has been observed on sub soils (Routson et al., 1977) and sandy soils (Sheppard et al., 1983), using a batch equilibration technique.

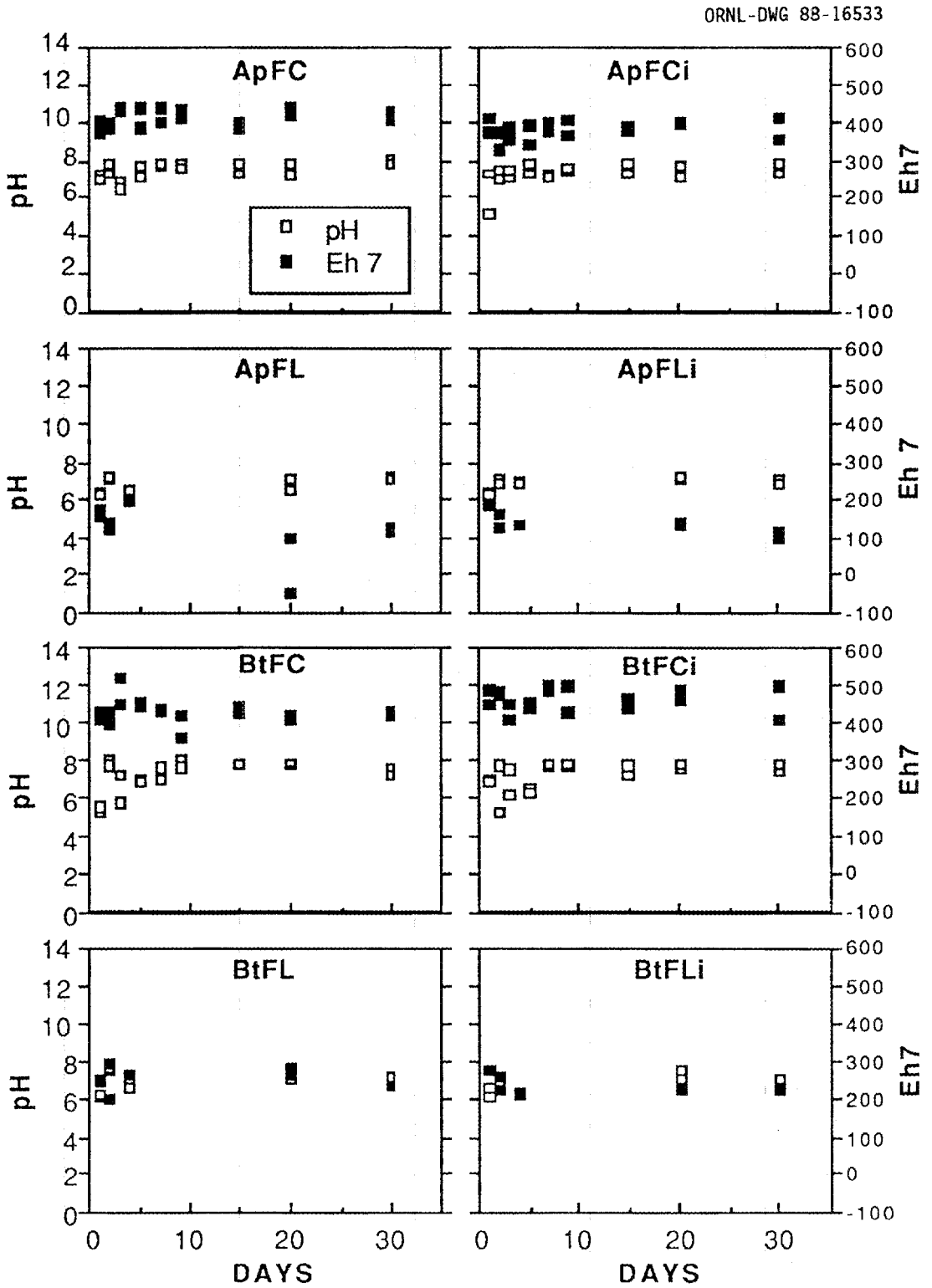

Fig. IV.3. Soil water Eh and pH for all kinetics samples as a function of incubation time.

The methodology used in this study to assess Tc sorption predicts Tc behavior under field conditions better than the traditional batch equilibrium technique. The sorption behavior of Tc observed here is in qualitative agreement with the results of a field study on Tc behavior in soil and vegetation by Garten and coworkers (1984). Comparison with their study is especially meaningful because the soil used for this work was collected from the field where their experimental plots were installed. They observed that $^{95m}TcO_4^-$ sprayed on the bare soil surface was rapidly sorbed. Extractability of Tc with $CaCl_2$ from the top 4 cm of the soil was 25-29% during the first 4 weeks of the experiment, then declined sharply to 8.7% between the fourth and ninth week. This decline in extractability could be related to the increase of rainfall that occurred between week 4 and 9 (increase of sorption with increase in soil water content).

The importance and the role of soil organic matter, microbial activity and soil water content in the mechanism of sorption will be dicussed in the conceptual model of Tc behavior in soil presented in Chapter V.

2. Kinetic parameters of Tc sorption

Several model equations have been used to study the adsorption of oxyanions by soil materials, among these, first-order kinetics, the Elovich model, and the parabolic diffusion model. These equations have been developed to model heterogeneous chemical reactions at the surface of soil material, and do not take into account possible changes of speciation or biotic processes leading to sorption. Since Tc sorption is in large part mediated by microbial processes (Fig. IV.1 and IV.2), the fit of Tc sorption data to these equations is a mathematical coincidence and does not imply that the mechanistic assumptions underlying the models are fulfilled. Consequently, the value of parameters derived from these

equations is limited to empirical descriptors of the overall sorption of Tc in the soils and under the conditions used in the experiment. Such kinetic parameters are nevertheless interesting to document, first, because the rate of the Tc sorption process should be an important factor to consider in the development of predictive models, and second, because there are no kinetic parameters for Tc in environmentally-relevant soil conditions reported in the literature.

The global kinetics of Tc sorption could be described in terms of a first-order reaction or a sum of pseudo first-order reactions. A first-order reaction implies that the reaction rate depends upon the concentration of only one reactant. In this case, given the small amount of Tc added to the soil, it is logical to consider that the reaction rate would depend solely on the concentration of TcO4- in the soil water; therefore :

$$- \Delta[TcO_4^-] / \Delta t = \lambda \ [TcO_4^-]$$ or its integrated form :

$$\ln \{ [TcO_4^-(t)] / [TcO_4^-(o)] \} = - \lambda t$$

where λ is the rate constant, and $[TcO_4^-]$ refers to the concentration in TcO_4^- at time o and t.

Sorption on ApFL can be described by a single first-order kinetics equation characterized by a rate constant of 0.435 days^{-1} (r^2= 0.82), corresponding to a half-life ($T = Ln2/\lambda$) of 1.59 days (Fig. IV.4B).

The rate of sorption of Tc in ApFC cannot be described by a single first order rate constant (Fig. IV.4A). There are alternative ways to describe such kinetics. The first alternative would be to describe the process as a sum of 2 first-order kinetics, each characterized by a given rate constant and compartment size. It would imply 2 consecutive processes, a very fast one followed by a slower one.

At the initial stage, the reaction proceeded at a fairly high rate, λ_1 = 0.0970, and T_1 = 7.14 days (r^2=0.97). After 26% of the Tc was complexed, which required 5 days, sorption proceeded at a much slower rate

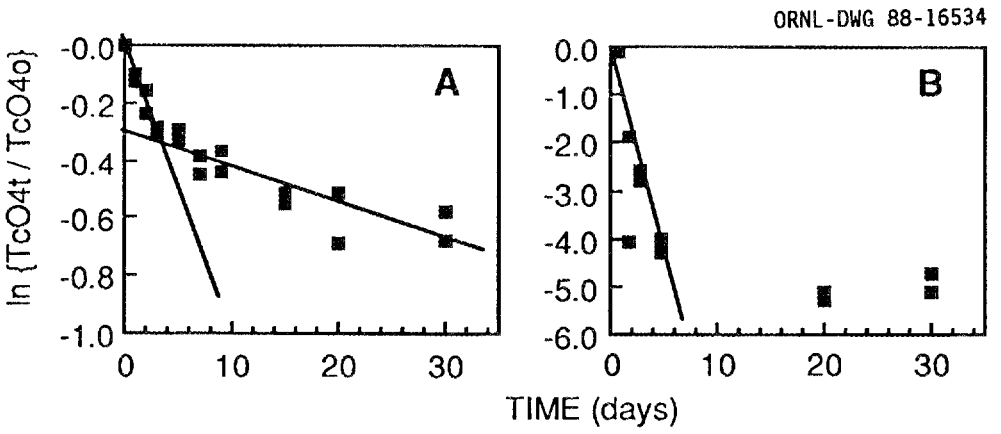

Fig. IV.4. First-order rate plot of the sorption of Tc in ApFC (A) and ApFL (B).

characterized by a λ_2 of 0.0122 days^{-1}, and a half-life of 56.81 days (r^2=0.86).

The second alternative would be to describe the rate of adsorption as a decreasing exponential function of the amount of material already sorbed (Elovich equation) :

$$\Delta(Tcs)/\Delta t = \alpha\, e^{-\beta\,(Tcs)} \qquad \text{or} \qquad Tcs = (\ln \alpha\beta + \ln t)\, \beta^{-1}$$

where Tcs is the amount of Tc already sorbed, and α and β are constants.

The Elovich model is a theoretical description of the sorption of gases on metal surfaces. In soil, it may describe a number of different processes (diffusion, activation of catalytic surfaces), and is mainly an empirical tool (Sposito, 1984). It has, however, been useful in predicting sorption of sulfate (Hodges and Johnson, 1987), and phosphate (Chien and Clayton, 1980) in soil.

The fit of the Elovich model to the experimental data of Tc sorption in ApFC yields α = 30.57, and β = 0.092478 (r^2=0.97).

The third alternative is the parabolic diffusion model (Cooke, 1966). It assumes that the reaction rate is controlled by the diffusion of ions to

the reactive sites, and is a function of the diffusion constant and the time of reaction such that : $Tcs = k \sqrt{t}$

The parabolic diffusion model provided a good fit to the experimental data for the first 10 days of sorption, i.e. before the reaction rate decreased. The parameter k is 11.74 with a r^2 of 0.95.

These three alternative ways to express the Tc sorption kinetics in ApFC would seem satisfactory. However, in spite of the good linear regression fit of all models, Fig. IV.5 shows that the Elovich equation [B] performs better than a sum of first-order kinetics [A] or the parabolic diffusion model [C]. The reason for this is that only the Elovich model allows sorption to reach an equilibrium with time.

In conclusion, sorption in ApFL and in ApFC cannot be modeled by similar parameters. Sorption in ApFL can be characterized by a single rate constant (0.435 $days^{-1}$) until complete disappearance of Tc. Sorption in ApFC is best described as a single process that occurs at a rate decreasing with time and eventually reaching 0 (Elovich model : α=30.57, β=0.092478), and is not well modeled as 2 consecutive processes.

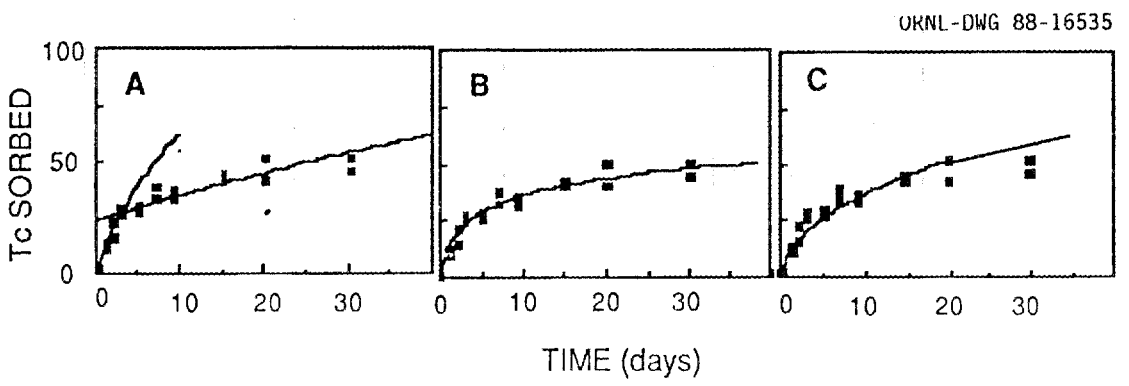

Fig. IV.5. Sorption of Tc in ApFC as modeled by (A) a sum of first-order kinetics, (B) the Elovich equation, and (C) the parabolic diffusion model. The black squares represent the experimental data points.

3. Effect of soil water content on the equilibrium distribution of Technetium in soil

As the contrast between Fig.IV.1 and Fig. IV.2 clearly shows, when organic matter and microbial activity are present, water content is the determining factor of the completeness of Tc sorption in soil. At field capacity, only 50% of the total Tc present in the sample was sorbed, whereas under flooded conditions, sorption was complete.

The amount of Tc sorbed and the values of Tc equilibrium distribution in soil were determined for a gradient of soil water content. To maintain a constant Tc concentration in the soil water, the samples incubated at lower soil moisture received a lower total amount of Tc.

Data for the Ap horizon are shown in Fig. IV.6. As the soil moisture increased, the amount of Tc sorbed and the equilibrium distribution of Tc in the soil increased. Sorption in the irradiated samples followed the same trend but the values were lower and somewhat erratic. Lower Tc sorption under reduced microbial activity indicated that soil water tension was not directly affecting TcO_4^- sorption, but that its effect was indirect, probably by creating a qualitative change in the microbial population.

Data on the sorption of Tc in the subsoil as a function of water tension are given in Table IV.1. Very little sorption took place and the amount of Tc sorbed was independent of the soil water content. A reduction of microbial activity did not affect the sorption process.

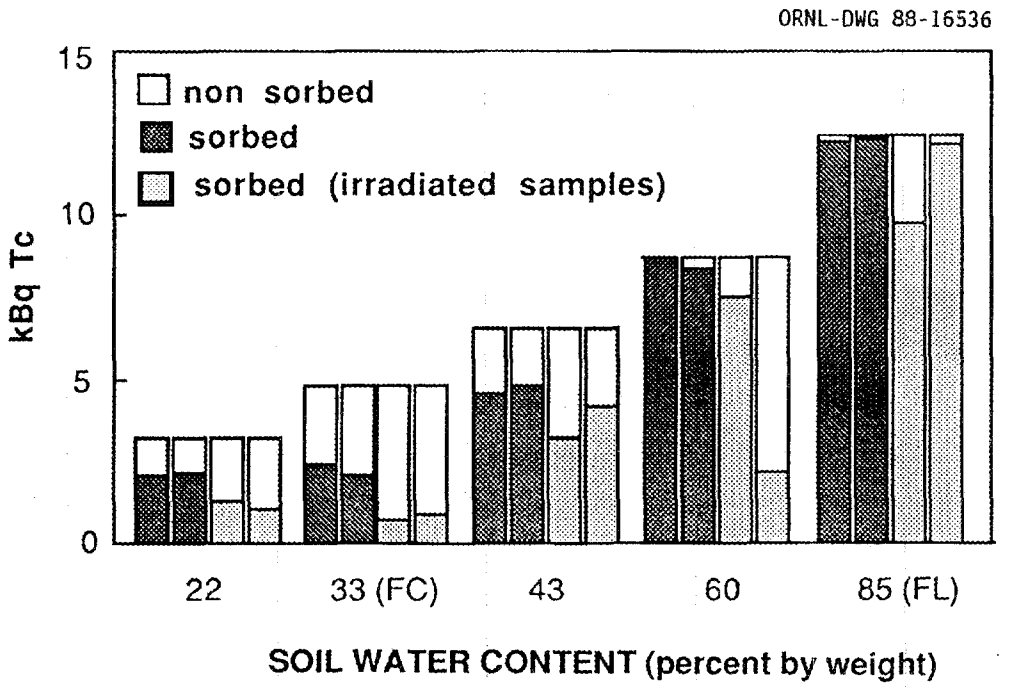

Fig. IV.6. Effect of soil water content on the equilibrium distribution of Tc in the Ap horizon soil. Two adjacent bars with the same pattern are duplicates.

Table IV.1. Equilibrium distribution of Tc in subsoil (Bt), and subsoil irradiated (Bti) incubated under various water tensions.

PW	15%		24%(FC)		45%		65%(FL)	
	Bt	Bti	Bt	Bti	Bt	Bti	Bt	Bti
Total Tc (Bq)	2871		4593		8580		12461	
% total Tc sorbed	0 0	0 0	0 12	10.4 14.1	1.9 5.8	0 0	8.0 2.5	0 8.8
Tc sorbed (Bq)	0 0	0 0	0 551	477 647	163 497	0 0	996 311	0 1096

4. Effect of Tc concentration on the equilibrium distribution of Tc in soil

In the top soil at field capacity (ApFC), as Tc concentration in the soil water increased, the amount of Tc sorbed increased, and the equilibrium distribution of Tc in the soil decreased. Irradiated samples showed the same trend but the amount of Tc sorbed was less (Fig. IV.7).

The relationship between the amount of material adsorbed and its equilibrium concentration in the soil water at a fixed temperature and pressure is called an adsorption isotherm. The adsorption equations developed by Langmuir and by Freundlich to quantitatively describe gas adsorption by solids have been used with some success in solid-liquid systems. The fundamental difference between the 2 equations is that the Langmuir model defines a maximum of material that can be adsorbed. This maximum corresponds to the total number of sites available for adsorption. The shape of the Langmuir isotherm is a typical saturation curve. The Freundlich model, on the other hand, does not predict a maximum adsorption capacity. Adsorption proceeds parabolically as concentration increases.

Technetium sorption data for the 3 lower concentrations (0.45, 0.82 and 1.23 kBq (mL soil water)$^{-1}$) were fitted by both the Langmuir and the Freundlich isotherms, with a r^2 of 0.970 and 0.973 respectively. Sorption values at an higher concentration (2.68 kBq (mL soil water)$^{-1}$) were accurately predicted by the Freundlich model but underestimated by the Langmuir isotherm. When sorption data for the higher soil water Tc concentration were included to determine the parameters of the Langmuir isotherm, the ensuing equation missed the data points for the lower concentration. Figure IV.8 presents the predictions of both models and the experimental data. The Freundlich equation described the process better. Therefore, at field capacity and within the range of concentrations used, there was no limit to the adsorption sites for Tc.

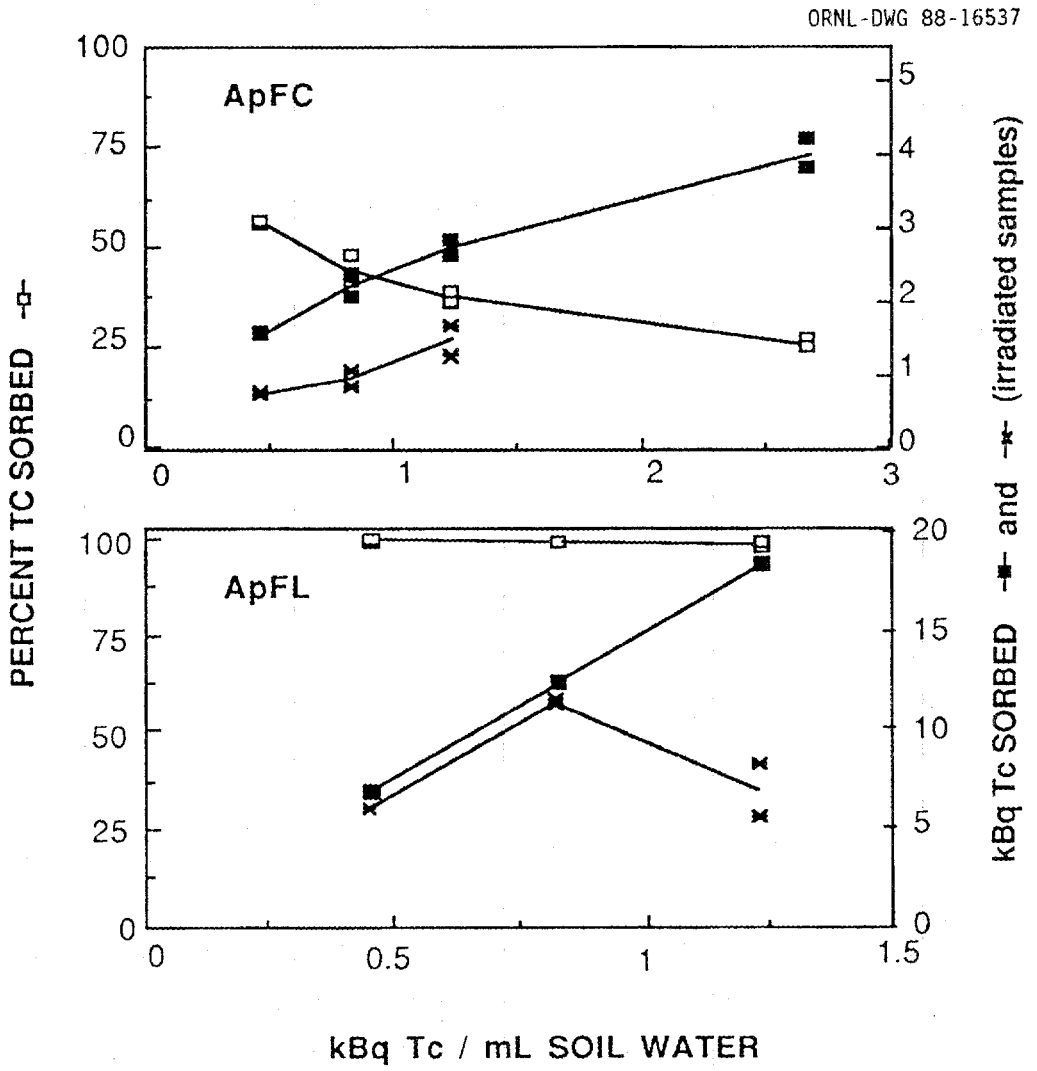

Fig. IV.7. Effect of Tc concentration in the soil water on sorption.

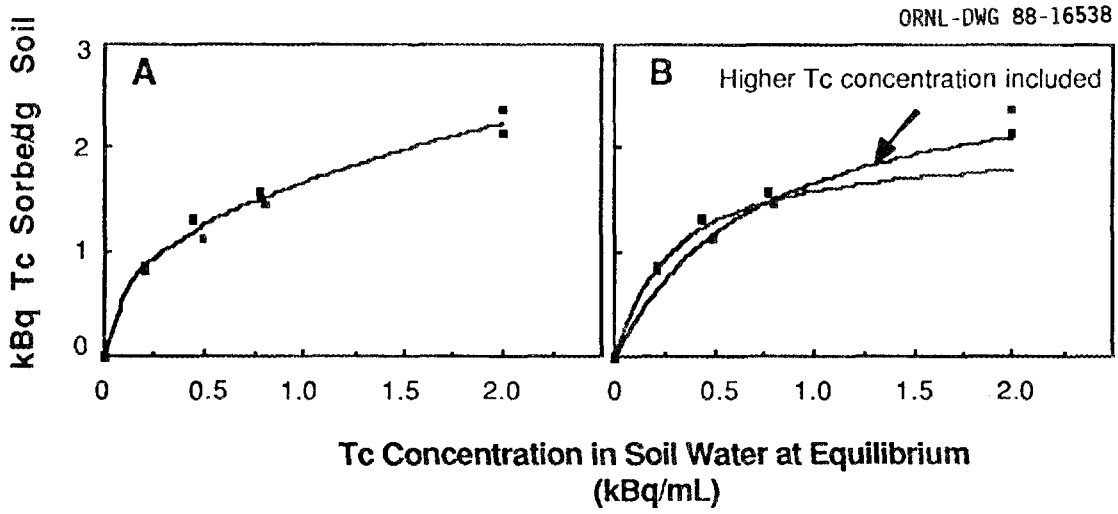

Fig. IV.8. Freundlich (A) and Langmuir (B) isotherms for Tc sorption in soil.

Equations and parameters for Langmuir and Freundlich isotherms are given in Table IV.2.

In the top soil under flooded conditions (ApFL), all the Tc present in the sample was sorbed regardless of the the initial Tc concentration (Fig. IV.7). The amount of Tc sorbed was not significantly less in the irradiated samples for Tc concentrations of 0.45 and 0.82 kBq (mL soil water)$^{-1}$), probably due to a regrowth of the microbial population during the 15 days of incubation. It was however significantly lower for the Tc concentration of 1.23 kBq (mL soil water)$^{-1}$ (Fig. IV.7).

Little Tc was sorbed on the Bt horizon, and there was no definitive trend of sorption as a function of Tc concentration for the samples incubated under field capacity and flooded conditions (Table IV.3).

In conclusion, in ApFC samples, the fraction of Tc sorbed decreased with the initial Tc concentration in the soil water. The amount of Tc sorbed as a function of Tc concentration is best described by a Freundlich isotherm with parameters of κ and n of 9.22 and 2.38 respectively. In contrast, sorption in Bt and ApFL samples were unrelated to the initial Tc concentration in the soil water. Indeed, in the case of Bt samples, little

Table IV.2. Parameters for Tc Langmuir and Freundlich adsorption isotherms, from ApFC sample data.

Equation	Parameters	r^2
x/m = amount of Tc sorbed per gram of soil C = equilibrium concentration of Tc in the soil water		
<u>Langmuir</u>		
$x/m = K\,C\,b\,(1+K\,C)^{-1}$	$K = 3.37 \times 10^{-3}$ $b = 204.08$	0.970
<u>Freundlich</u>		
$x/m = \kappa\,C^{1/n}$	$\kappa = 9.219$ $n = 2.38$	0.973

Table IV. 3. Technetium equilibrium distribution and amount of Tc sorbed in the subsoil horizon as a function of Tc concentration and soil treatment. Two columns under the same heading are duplicates.

Treatment	Tc Conc. (Bq/mL)	Total Amount Tc (Bq)	Amount Tc Sorbed (Bq)		Percent Tc Sorbed	
BtFC	455	2548	280	0	11.0	0.0
	825	4620	656	817	14.2	17.7
	1232	6899	455	351	6.6	5.1
BtFCi	455	2548	558	214	21.9	8.4
	825	4620	665	914	19.8	7.5
	1232	6899	517	772	7.5	11.2
BtFL	455	6779	294	145	4.3	1.3
	825	12292	405	12	3.3	0.1
	1232	18356	385	440	2.1	2.4
BtFLi	455	6779	87	0	1.28	0
	825	12292	491	0	4.0	0.0
	1232	18356	0	0	0.0	0.0

Tc was sorbed at all concentrations, and in the case of ApFL, all the Tc present was sorbed at all concentrations.

These observations indicate that Tc sorption in the soil is more affected by soil horizon (Ap vs. Bt) and soil water content (FC vs. FL) than by Tc concentration in the soil water. Therefore, the general behavior of Tc in a given soil can be predicted in spite of limited information on the amount of Tc present. This is particularly interesting because the uncertainty attached to the amount of Tc present in the soil following an accidental release is generally very high.

The increase in the amount of Tc sorbed with an increase in Tc concentration in the soil water demonstrates that the availability of "sorption sites" was not a limiting factor for Tc sorption in ApFC within the range of the experimental conditions. Therefore, the attainment of a sorption maximum with time cannot be attributed to a saturation phenomenon.

5. Role of the soil organic matter as a sink for sorbed Tc

The soil organic matter was extracted in 3 successive fractions of increasing pH : pH 9, 10, and 11. Preference was given to 3 fractions rather than to the 2 classical fulvic acids and humic acids fractions principally for methodological considerations. The separation of humic acids from fulvic acids involves a harsh chemical treatment (acid precipitation) and also more handling of the organic extract, which could increase the risk of a change of Tc species during the procedure.

Moreover, there is no theoretical basis for the division of the organic matter into these 2 fractions. The soil organic matter is a mixture of polymers with a continuum of size and density of functional groups. Typically, as the molecular size of the polymers increases the density of their functional groups decreases. Fulvic acids are characteristically low molecular weight molecules with a high density of functional groups, and humic acids are typically high molecular weight molecules with a lower density of functional groups. The distinction between these 2 fractions is based on solubility characteristics. Humic acids are soluble in alkali and insoluble in acid, whereas fulvic acids are soluble in both (Stevenson, 1982).

In this study, the organic matter was divided into fractions operationally defined by their pH of extraction. In the first fraction (pH9), one expects organic matter rich in functional groups to be present. Indeed, the role of the extractant (NaOH) is to saturate the functional groups with Na, "unfold" the organic matter, and solubilize it. As pH increases, or as the NaOH concentration increases, the organic matter more refractory to extraction (i.e. containing less functional groups) is recovered. Therefore the fractions obtained at pH 10 and 11 have a increasingly lower density of functional groups. The percentage of organic matter not extracted (present in the soil "residue" after organic matter extraction) and characteristics of the 3 fractions are given in Table IV.4.

Table IV.4. Completeness of extraction and characteristics of the soil organic matter extracts.

Treatment	% of OM not extracted	pH of the extractant	CA[a]	E4/E6[b]
ApFC&i	36	9	500 ± 90	5.9 ± 1.3
		10	232 ± 54	4.8 ± 1.7
		11	107 ± 21	3.8 ± 0.9
ApFL&i	47	9	317 ± 72	4.9 ± 1.4
		10	372 ± 66	4.6 ± 0.7
		11	144 ± 24	4.0 ± 1.2
BtFC&i	21	9	183 ± 56	4.6 ± 1.5
		10	ND[c]	-
		11	-	-
BtFL&i	19	9	152 ± 75	4.3 ± 1.4
		10	ND	-
		11	-	-

[a]Carboxylic acidity at pH 7 was measured by precipitation with cobalthexamine (pp. 26). It is expressed here as the total amount (μeq) of cobalthexamine that precipitated with the soil organic matter extract.

[b]E4/E6 is the ratio of the optical density of the organic matter at 465 and 665 nm. It decreases inversely with the size and the degree of condensation of the organic material.

[c]ND = CA too low to be determined, but the coloration of the extract indicated the presence of humic material.

The objectives of the study of Tc association with the soil organic matter were to determine (1) if Tc sorption can be equated with Tc complexation with the soil organic matter, (2) if there is a change in the pattern of Tc distribution among the soil extracts as a function of time and Tc soil water concentration, and (3) if Tc is predominantly associated with the low molecular weight organic fraction as was suggested by Stalmans (1986).

Proportion of sorbed Tc associated with the soil organic matter

The percentage of sorbed Tc recovered in the organic matter extracts is large. In all Bt samples, the sum of Tc in the 3 organic matter extracts is close to 100% of the sorbed Tc (data not shown).

In Ap samples, the recovery of sorbed Tc was also high. Figure IV.9 shows that 60 to 75% of the Tc sorbed was recovered in the organic matter extracts. The 35 to 40% of sorbed Tc that was not extracted (i.e. that remained in the soil residue) could represent inorganic Tc precipitates, or Tc associated with non-extracted organic matter. Indeed, up to 47% of the total organic matter (Table IV.4) was not extracted by the highest NaOH concentration (0.1 M). It is therefore possible that Tc would be associated with that fraction. Under flooded conditions, the activity of the anaerobic microflora could promote the formation of inorganic precipitates as TcO_2 or Tc_2S_7 by direct reduction of Tc(VII) to Tc(IV), or H_2S production.

In conclusion, a large proportion of the sorbed Tc (a minimum of 60 to 75%) can be explained by Tc association with the soil organic matter. The importance of the soil organic matter as a sink for sorbed Tc was suggested by numerous observations that Tc sorbed in the soil under field (Garten et al., 1984; Garten et al., 1986a; Bondietti and Garten, 1986) and laboratory (Landa et al., 1977; Stalmans et al., 1986) conditions was recovered (to various degrees) by diverse oxidizing agents (H_2O_2, NaOCl) and alkaline solutions (NaOH, Na_2CO_3).

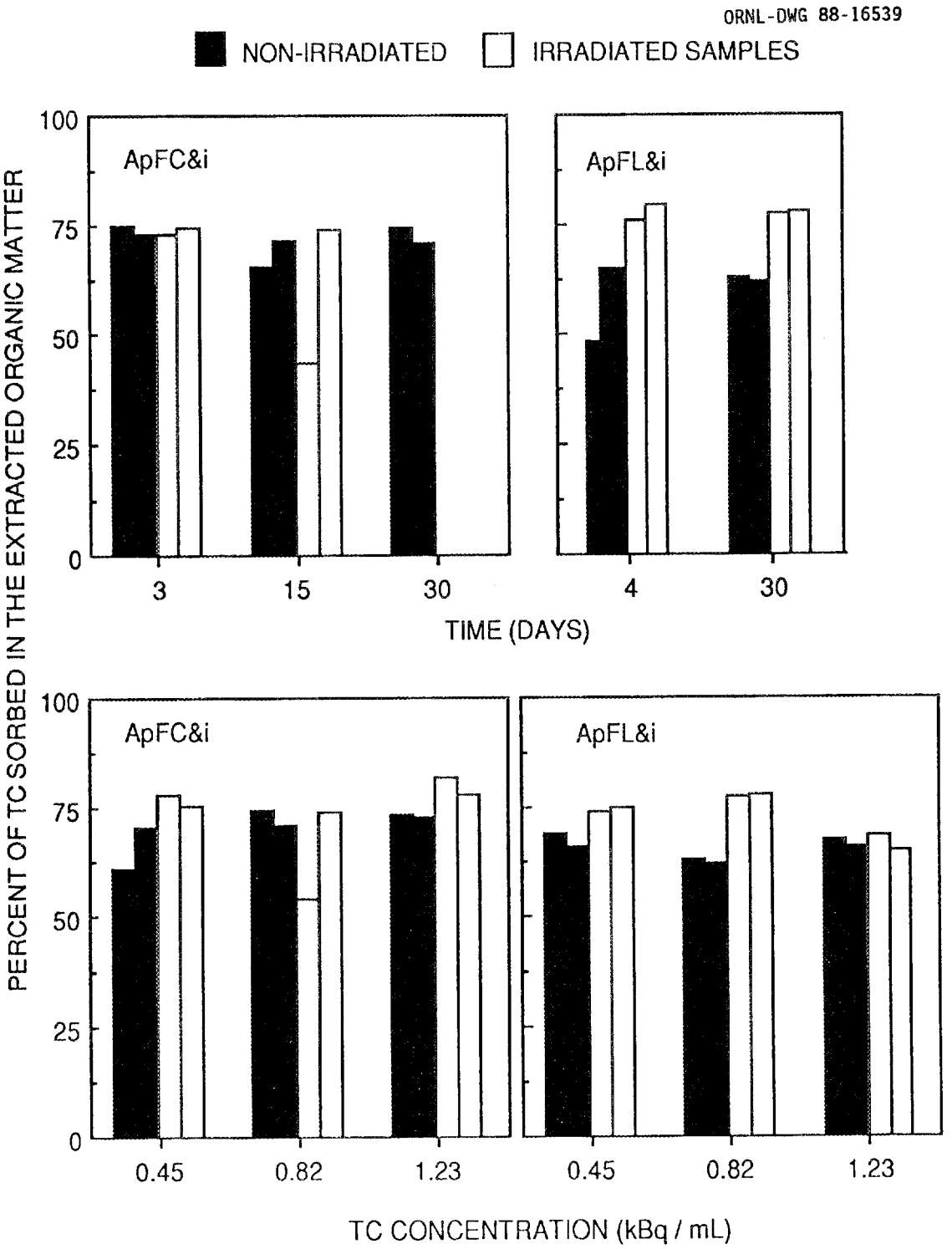

Fig. IV.9. Percent of Tc sorbed recovered in the organic matter extracts. Adjacent bars with the same pattern are duplicates.

Wildung et al. (1986), based on the results of a multiple regression analyses of sorption data against key soil properties, suggested that the major factors influencing Tc sorption were oxidic Fe at earlier times and organic C at later times during the equilibration period. In the experiment presented here, Tc complexation was the dominant factor determining Tc sorption during the entire period of incubation; the fraction of sorbed Tc recovered with the soil organic matter was high at all times and concentrations.

Pattern of Tc distribution in the soil organic matter extracts as a function of time and Tc concentration in the soil water

In Bt samples, 80 to 100% of the Tc sorbed was recovered in the first organic matter extract (pH9) (data not shown).

In Ap samples, as expected, the amount of Tc recovered in the extracts increased with time (Fig. IV.10) and with Tc concentration in the soil water (Fig. IV.11). The distribution of Tc among the organic matter extracts, however, presented 3 striking characteristics. The first characteristic is that the amount of Tc recovered in the first extract (pH9) was usually the largest. The second characteristic was that Tc distribution among extracts in ApFC samples differed from that in ApFL samples. In ApFL samples, the second extract contained as much or more Tc than the first one. The third characteristic is that, with time or Tc concentration, the amount of Tc increased proportionally in all extracts, so that the pattern of Tc distribution among extracts remained identical. Figure IV.12 shows the typical distribution of sorbed Tc among organic extracts of ApFC and ApFL samples. The low standard deviations of the pooled means indicate the lack of change in the distribution of Tc among organic extracts over time and with Tc concentration.

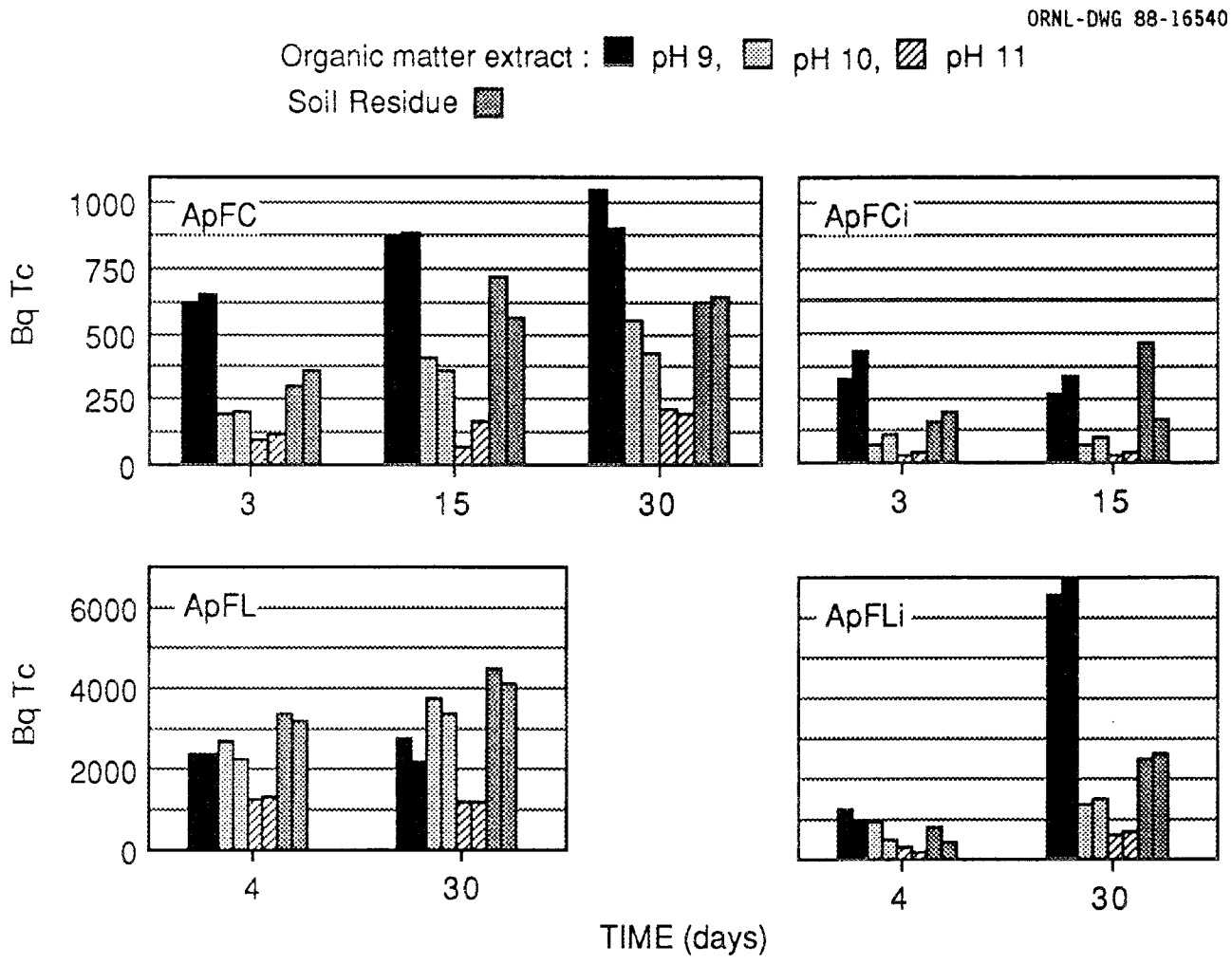

Fig. IV.10. Distribution of Tc among the soil organic matter extracts and the soil residue as a function of time and treatment. Adjacent bars with the same pattern are duplicates.

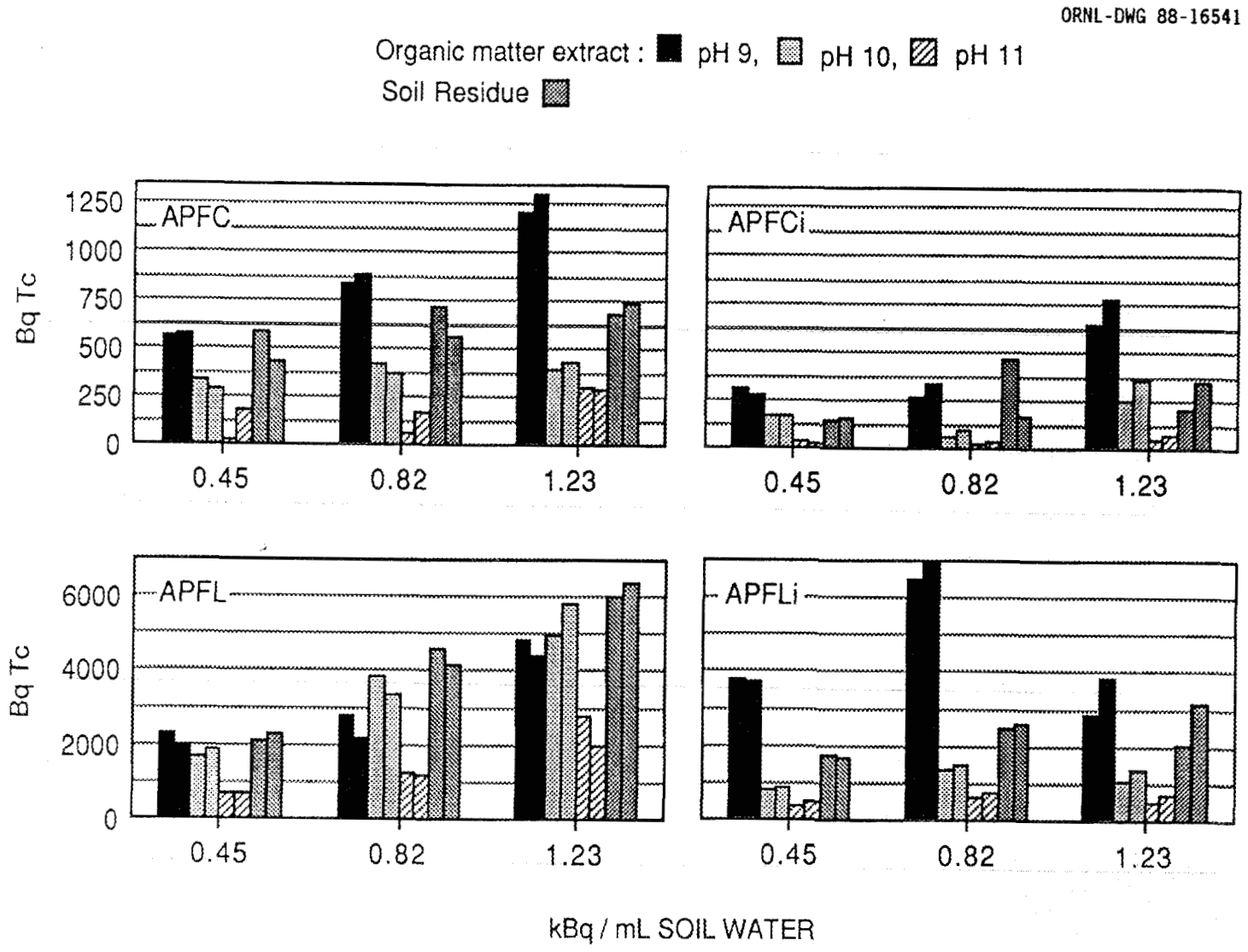

Fig. IV.11. Distribution of Tc among the soil organic matter extracts and the soil residue as a function of soil water Tc concentration and treatment. Adjacent bars with the same pattern are duplicates.

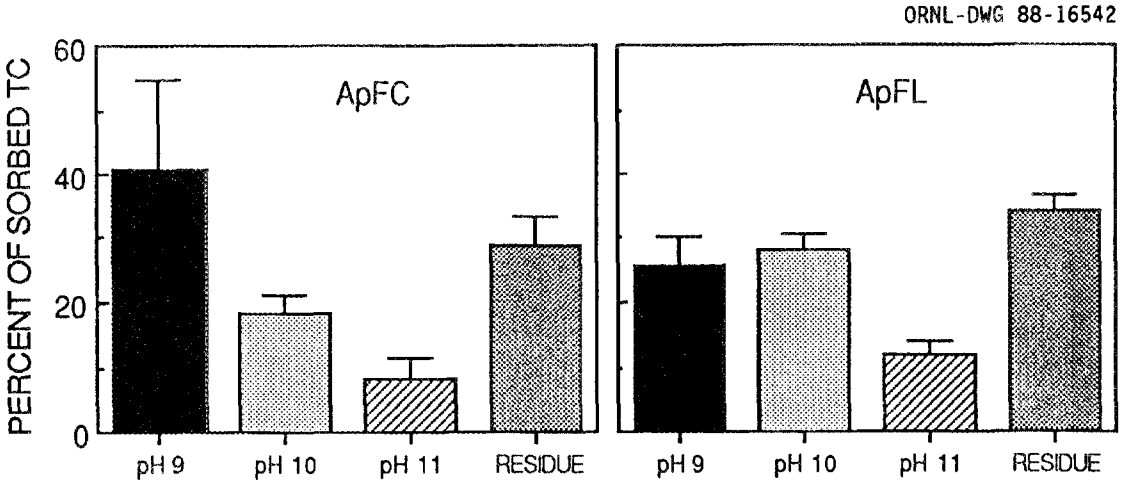

Fig. IV.12. Pattern of distribution of sorbed Tc among the organic matter extracts and the soil residue for ApFC and ApFL samples. The graph presents the pooled means and the standard deviations for day 3, 15, 30 and concentration 0.45, 0.82, 1.23 for ApFC extracts (n=6), and for day 4, 30 and concentration 0.45, 0.82, 1.23 for ApFL extracts (n=5).

The first 2 characteristics of Tc distribution among organic matter extracts (abundance of Tc in the first extract and difference in Tc distribution among extracts between ApFC and ApFL samples) can be related to the carboxylic acidity of the extracts. Indeed, the ratio of the percentage of sorbed Tc present in an extract over the amount of carboxyl groups (CA) present in that extract was fairly constant (Table IV.5). This relatively constant ratio suggests that the reactivity of the organic matter with Tc was determined by the amount of carboxyl groups it carried, and therefore, explains the high Tc recovery in the first extract (high amount of carboxyl groups present) and the difference between ApFC and ApFL samples. At pH 9, more Tc was recovered in the first extract of ApFC than in that of ApFL, however, in the pH9 extract of ApFC, there was also a larger amount of carboxyl groups than in that of ApFL. It is important to note that carboxylic acidity was determined at pH 7, which was the prevalent pH in the soil water of all samples, therefore, CA measured on the extracts was representative of the free carboxyl groups present in the soil.

Table IV.5. Ratio (R) of the percentage of sorbed Tc present in an extract (% Tc sorbed) over the amount of carboxyl groups (CA) present in that extract

Extract		% Tc sorbed	CA (μeq)	R
ApFC	pH9	41.0 ± 13.7	500 ± 90	12.2
	pH10	18.3 ± 2.3	232 ± 54	12.7
	pH11	8.6 ± 3.4	107 ± 21	12.4
	residue	18.6 ± 4.6	ND*	
ApFL	pH9	25.1 ± 4.6	317 ± 72	12.6
	pH10	27.4 ± 2.3	372 ± 66	13.5
	pH11	11.4 ± 1.7	144 ± 24	12.6
	residue	34.3 ± 2.3	ND	

*ND = not determined

The observation that reactivity of the organic matter with Tc was determined by the amount of carboxyl groups it carried, rather than by their density implies that a small molecule with a high density of functional groups (fulvic acid type) has the same reactivity with Tc as a large molecule with a low density of functional groups (humic acid type) if the total amount of groups is identical. Therefore, Tc was predominantly recovered in the pH9 extract because this fractions contained a large amount of functional groups. Technetium association with the molecules of the pH9 extract was, however, not preferential. If the association were preferential, the reactivity of the molecules would have been a function of the density of functional groups, and the ratio (percentage of sorbed Tc over CA) would have dropped at the higher extraction pH (pH 11).

The term "sorption" was used so far as "disappearance of Tc from solution". Based on the high proportion of sorbed Tc recovered with the

organic matter and on the relationship between Tc sorbed and carboxylic groups, sorption can be equated to Tc reaction with carboxylic groups of the soil organic matter. This work was not designed to study the nature of Tc reaction with carboxyl groups, however, it suggests that Tc was complexed with these groups by chelation or coordinative bonding. Indeed, Tc retained by the organic matter as exchangeable cation (reduced Tc could be charged positively) would have been released in the acidic fraction (0.075 M HCl) preceding the successive alkaline extractions because carboxyl groups are not dissociated (no negative charge) at acidic pH. Further research is necessary to determine the nature of Tc-organic matter complexes.

The third characteristic of Tc distribution among organic matter extracts (i.e., absence of change in the pattern of Tc distribution among the soil extracts as a function of time, Fig. IV.12) suggests that the *kinetics* of Tc association with the organic material was the same for the different extracts. If this were not the case, one would have expected a preferential binding early on with the more reactive fraction, and possibly, a ligand exchange over time.

The proportional increase of Tc in all the organic fractions as the Tc concentration in the soil water increased clearly demonstrates (Fig. IV.11) that the availability of "sorption sites" was not a limiting factor for Tc association with a particular extract. Therefore, the association of Tc with the organic material of the pH10 extract, for example, cannot be attributed to the saturation of the sorption sites present in the pH9 extract. These data confirm the previously discussed isotherm plots.

What determines the distribution of Tc between soil organic fractions is the contribution of each fraction to the total amount of functional groups. The predominant association of Tc with the low molecular weight (LMW) organics is due to the fact that these compounds carry a large proportion of the total amount of functional groups. However, if the ratio of high molecular weight (HMW) to LMW is increased, the contribution of the HMW to the total amount of functional groups would also be increased, and HMW would have the potential to

complex a larger proportion of Tc. A prediction of these results is that Tc distribution between LMW and HMW is a function of the ratio between HMW and LMW in the soil. In soils with high ratio (e.g. grassland soils : humic acids/fulvic acid ratio up to 2.5 - Stevenson, 1982), a larger proportion of Tc would be associated with the HMW than in soil with low HMW/LMW ratio (e.g. forest soils : humic acids/fulvic acid ratio close to 1).

The distribution of Tc between HMW and LMW organic material has direct implications on the potential of remobilization of sorbed Tc. First, HMW have a longer mean residence time in the soil than do LMW; they are less susceptible to microbial attack, thus, less rapidly mineralized and solubilized. Therefore, Tc associated with HMW will have a lower potential of remobilization than Tc associated with LMW. Second, as will be discussed in the next section, the intrinsic stability of HMW-Tc complexes and LMW-Tc complexes may be different.

In summary, (1) a large fraction of the Tc sorbed was associated with the soil organic matter, (2) Tc association with the soil organic matter was the predominant mechanism of Tc sorption during the entire sorption process, (3) the kinetics of Tc association was the same with all the organic fractions, (4) the reactivity of Tc with the soil organics was directly proportional to the amount of carboxyl groups they carried, this observation (a) explains that Tc association with the LMW fraction of the soil organic matter was predominant and (b) suggests Tc complexation with the free carboxyl groups of the organic matter, and (5) Tc distribution between LMW and HMW organic fractions is determined by the ratio between HMW and LMW present in the soil.

6. Chemical form of Tc in the soil water

Technetium present in the soil water of ApFC&i and Bt samples migrated on a thin layer chromatography sheet like TcO_4^-. Technetium

concentration in the soil water of ApFL&i samples was too low to produce reliable results using this procedure.

The failure to observe an association of Tc with dissolved organics was perhaps due the low amount of dissolved organics in the soil water (i.e., too low to be measurable). However, based on the pattern of association of Tc with the organic material (proportional to the amount of functional groups carried), one could expect that if the dissolved organic content of the soil water were higher, this material (mostly fulvic acids) would complex significant amounts of Tc. Technetium association with dissolved organics is important in 2 respects. First, TcO_4^- is the only bioavailable form of Tc (Van Loon, 1986a), therefore, dissolved Tc-organic matter complexes will not be taken up by plants. Second, the pattern of migration of the Tc-organics complexes through the soil profile could differ substantially from that of the mineral TcO_4^- due to differences in electric charge and molecular size.

7. Kinetics of release of sorbed Tc upon drying

Ap horizon At equilibrium, about 50% and 100% of the total Tc was sorbed in ApFC and ApFL, respectively (Fig. IV.1 and IV.2, pp. 50-51). As shown in Fig. IV.13, air-drying the samples resulted in a release of some of this sorbed Tc. About 50% of the Tc sorbed in ApFC and 75% of the Tc sorbed in ApFL returned to solution. The release occurred within a few days and no measurable additional release took place in the following 85 days of the experiment (Fig. IV.13).

The release observed here is larger and more rapid that what could be expected based on the 2 existing studies on the reoxidation of sorbed Tc. Bondietti and Garten (1986) studied the release of sorbed Tc from soil by equilibrating sieved contaminated soil with an anion-exchange resin. The resin was frequently changed, and over the 15 day period of the experiment a total of 20% of the sorbed Tc was recovered from the resin. However, since Tc recovery from the resin was only partial, the measure

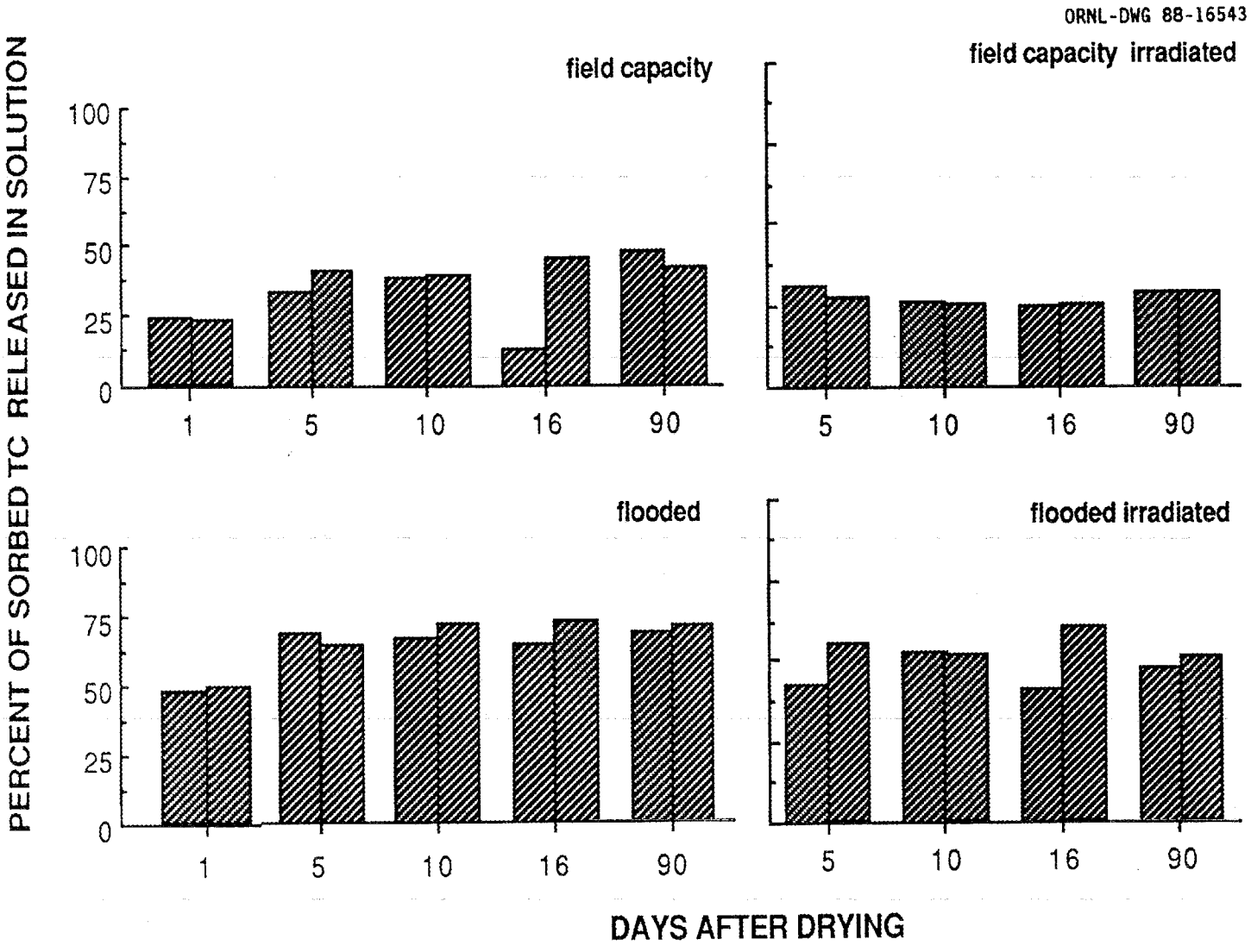

Fig.IV. 13. Release of sorbed Tc from Ap samples after air-drying. Adjacent bars are duplicates.

underestimated the amount of Tc actually released from the soil. The difference in magnitude and rate of Tc desorption between their results and the results presented here can also be explained by the harsher reoxidation conditions used in this experiment : air-drying of the soil rather than removal of TcO_4^-.

Sorbed Tc, in this study, was predominantly associated with the soil organic matter. A maximum of 25 to 40% of the sorbed Tc was possibly in another chemical form, as insoluble TcO_2 or Tc-sulfide. The release of sorbed Tc from the soil, therefore, corresponds mainly to a reoxidation of Tc-organic matter complexes. Stalmans (1986) observed the reoxidation of TcO_2 precipitates and dilute solutions of Tc-organic matter complexes maintained under continuous air-saturation. The half-time values determined for TcO_2 reoxidation were 5, 10, and 120 days, depending on the nature of the reducing agent used to generate the precipitate. The rate of Tc release from the Tc-organic matter complexes was variable and dependent on the nature of the organic material. Reoxidation of Tc-humic acids complexes proceeded with half-values of 7 days (40% of the Tc-complexes) and 114 days (60%). Reoxidation from Tc-fulvic acids complexes proceeded with a half-value of 120 days. The data presented here suggest that a large amount (50 to 75%) of the Tc-organic matter complexes reoxidized rapidly, and that the remaining sorbed Tc did not reoxidize or reoxidized extremely slowly. The reason why the magnitude and rate of Tc release is higher than could be predicted from Stalmans' observations is not clear.

Stalmans (1986) results' indicated that fulvic acids are more resistant to oxidation than humic acids. The higher stability of Tc-low molecular weight organic complexes could explain why ApFL samples released more Tc than did ApFC samples. Indeed, ApFL samples which had 25% of their Tc-organic complexes in the pH9 extract released a larger proportion of their sorbed Tc than did ApFC samples which had 50% of their Tc-organic complexes in the pH9 extract (75 and 50% of Tc sorbed released, respectively).

What these three studies demonstrate is that Tc sorption in the soil is not an irreversible process. Sorbed Tc partially desorbs under oxidizing conditions (dry soil, fire) and is resolubilized as TcO_4^-. This study suggests that the rate of reoxidation and the amount of Tc remobilized can be considerably higher than previously observed. The reoxidation rate of Tc-organic matter complexes is an important parameter to assess the long-term mobility and bioavailability potential of Tc in the soil system. If the reoxidation kinetics are slow, Tc-organic matter complexes will remain in that form as long as the organic matter is not mineralized, and the potential for Tc remobilization is limited. If the reoxidation kinetics are rapid, the potential for Tc remobilization is high. Because of (1) a lack of an agreeing body of data on the reoxidation rate of sorbed forms of Tc, and (2) the importance of this parameter in long-term risk assessment for Tc, it is critical that more research be done in this area.

Bt horizon When Bt samples contaminated with Tc were dried and rewetted with 5 mL of water, about 30% of the water added was recovered by centrifugation. In this 30%, 50% of the total Tc was present (Fig. IV.14). This means that the concentration of Tc in the soil water was higher than that expected if one assumes a homogeneous distribution of Tc in the soil water; i.e. Tc was repelled by the soil and eluted from the soil faster than the water. This phenomenon is known as "negative adsorption" and has been demonstrated for Cl^- and PO_4^- (Bohn et al., 1985). It is explained by the fact that upon wetting a clay mineral, water is retained by the silicates for their hydration. Therefore, water moves faster at the center of the soil pores than on the sides, where it comes in contact with the silicates. Since mineral surfaces are negatively charged, they electrically repulse the negatively charged ions towards the center of the pores, causing them to elute with the faster-moving water. The implication of such a behavior is that, if a light rain occurs, Tc deposited on a dry soil rich in clay minerals will move through the soil profile with the water front.

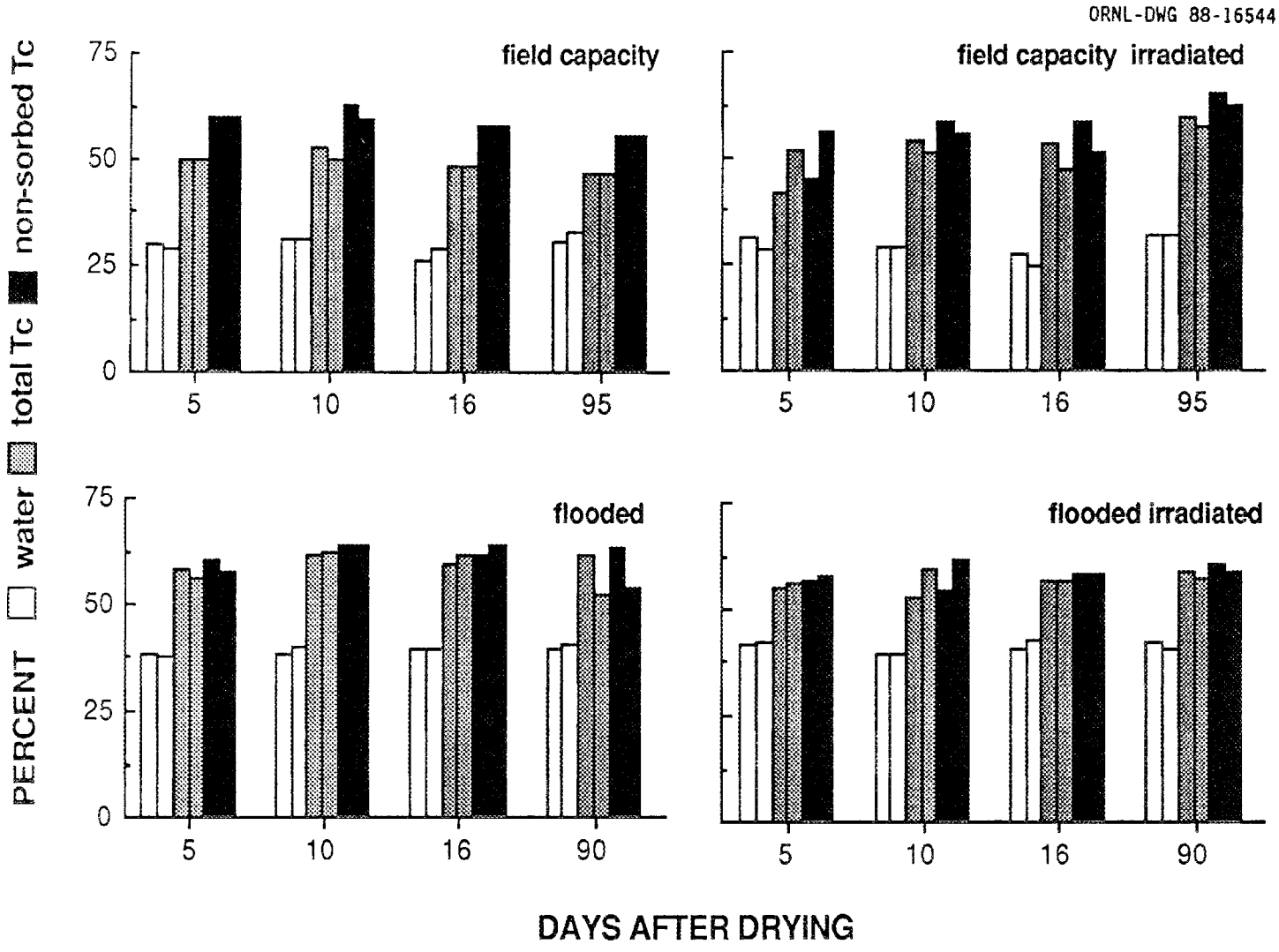

Fig. IV.14. Negative adsorption of Tc from air-dried Bt samples. Adjacent bars with the same pattern are duplicates.

8. Effect of drying / rewetting regime on Tc sorption

Figures IV.15 and IV.16 illustrate the change in Tc sorption in samples which were incubated at an initial water tension (field capacity or flooded), dried, and re-incubated at the same or a different water tension. In the Bt samples, little sorption took place under all conditions (Fig. IV.16). In the Ap samples, the soil : water equilibrium distribution of Tc depended solely on the prevalent water tension (Fig. IV.15). Under flooded conditions, sorption was always complete. Under field capacity conditions, about 50% of the total Tc was sorbed to the soil, regardless of the previous conditions of incubation. In ApFL, the changes in Tc equilibrium distribution with soil water content imply that at least 50% of the sorbed Tc was desorbed upon drying the soil, since Tc sorption decreased from 100% under flooded conditions to about 50% at field capacity.

Tc behavior under a drying/rewetting regime illustrates the combined effect of Tc desorption and sorption that might happen under field conditions. The fraction of Tc sorbed in the soil is determined primarily by the soil water content. When the soil dries, reoxidation takes place. Reincubation under a given water content re-establishes the equilibrium distribution characteristic of that water content. The drastic difference between this experiment and field conditions is that, in the field, leaching of Tc from the soil would occur at each drying/rewetting cycle. The amount of Tc available for sorption would thus be lowered each time the soil was rewetted. Because the proportion of Tc sorbed in ApFC increases as the Tc concentration in the soil water decreases, the speed of Tc disappearance from the soil would be slightly reduced. In the long term, however, as the drying/rewetting process is repeated, Tc will be leached until only Tc-organic matter complexes that are very resistant to reoxidation remain in the soil.

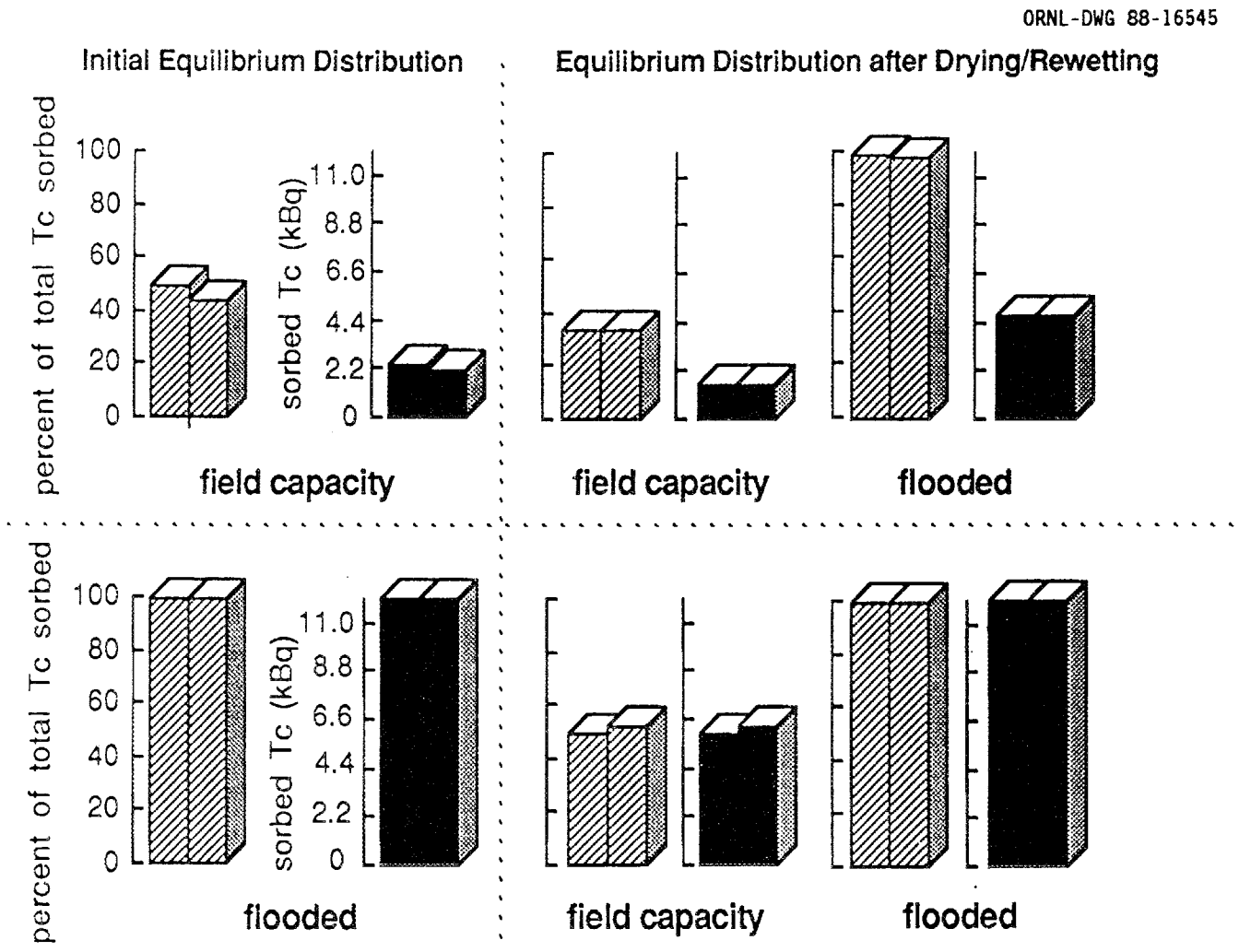

Fig. IV.15. Effect of drying / rewetting regime on Tc sorption in Ap samples.

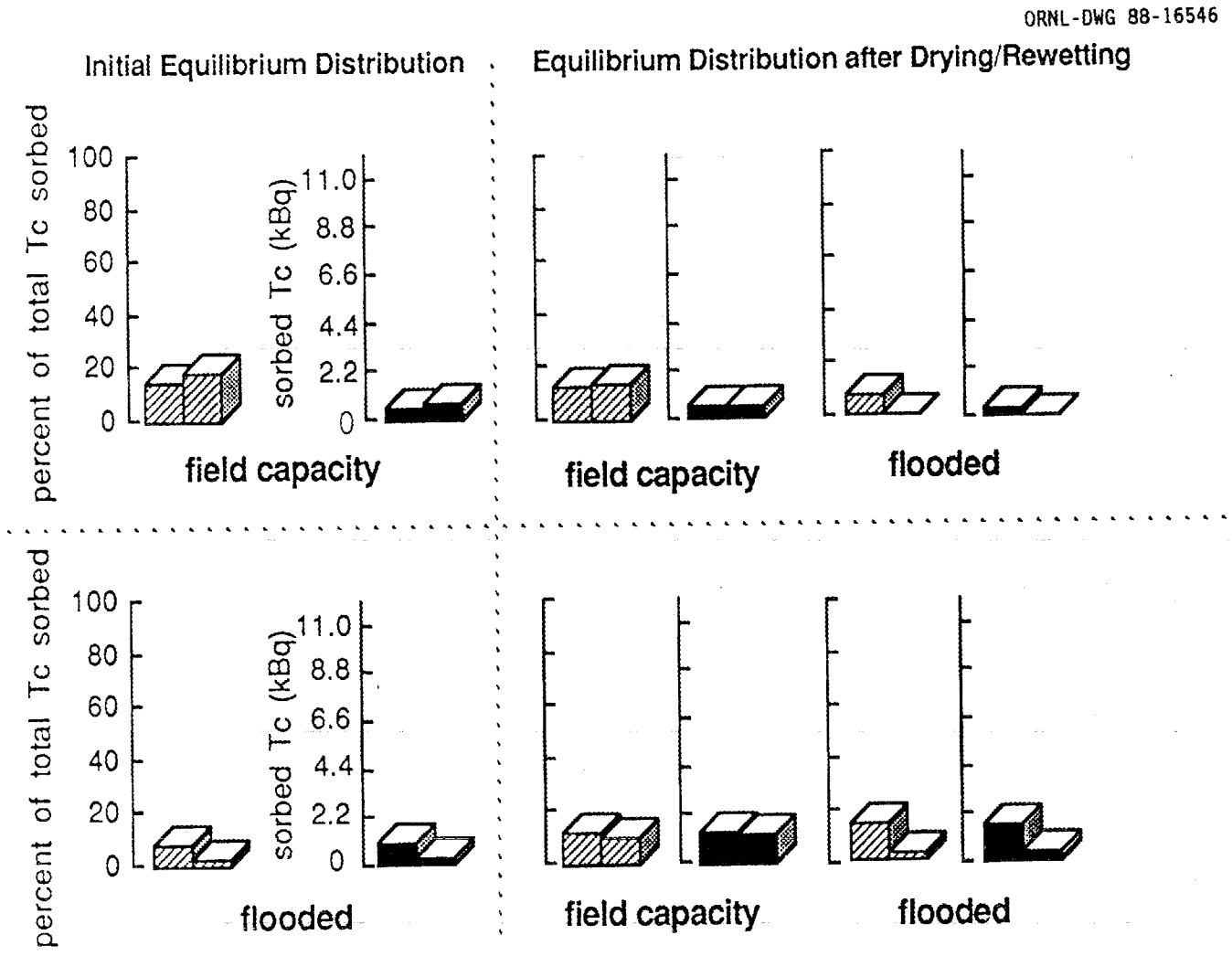

Fig. IV. 16. Effect of drying / rewetting regime on Tc sorption in Bt samples.

CHAPTER V

CONCLUSIONS

A. Conceptual Model of Tc Behavior in Soil

From the data on Tc behavior in Ap and Bt horizons presented in Chapter III and IV, a conceptual model of Tc sorption in soil was developed. Since this model is developed from observations on only 2 horizons of a soil, its generalization to soils typical of temperate regions requires caution. For example, both Ap and Bt horizons contained sufficient organic matter to coat Fe and Al oxides and therefore, to prevent contact of Tc with these soil components.

Low sorption on Bt is due to its low organic matter content

In this study, the contrast in Tc sorption between the Ap and Bt horizons and the recovery of sorbed Tc in the soil organic matter underlined the important role played by the soil organic matter in Tc sorption. The role of the soil microbial activity was illustrated by the lack of sorption in the Bt horizon and the reduced sorption in gamma-irradiated soils. A positive correlation between Tc sorption and soil organic matter content has often been observed (Landa et al., 1977; Sheppard et al., 1983; Mousny and Myttenaere, 1981; Wildung et al., 1986). Therefore, as a generalization, soils very poor in organic matter and supporting a low bacterial population (Bt type) would have a low sorption capacity for Tc. Conversely, soils presenting some organic matter and supporting a large microbial population (Ap type) would have a high potential to sorb Tc. In these soils, Tc sorption can be explained by the processes discussed below.

Pertechnetate is reduced by the anaerobic microbial population of the soil

TcO_4^- $\xrightarrow{\text{anaerobic bacteria}}$ $Tc(<VII)$

Data presented in chapter III indicated that the anaerobic microbial population of the soil had the potential to reduce Tc and to promote its complexation with organics. Aerobic bacteria, in contrast, did not show this potential.

Data presented in chapter IV indicated that Tc sorption in soil (1) was strongly diminished when soil microbial activity was reduced by gamma-irradiation, even when the soil was flooded, and (2) increased with increasing the soil water content. These 2 observations further suggest a direct role of the anaerobic bacterial population in the sorption process.

If reducing conditions by themselves were sufficient to promote Tc reduction and its complexation with the soil organic matter, a high sorption would have occurred in the irradiated samples as well. (The samples destined for gamma-irradiation had been incubated under flooded conditions for 10 days before irradiation, and their redox potential, after irradiation, was similar to that of the non-irradiated flooded samples (Fig. IV.3, p. 53).) Even if the predominance diagram of Tc chemical forms vs. Eh and pH indicates that the Tc(IV) form should predominate, it will not necessarily be so if the kinetic of the process is infinitely slow. Furthermore, the reduction of TcO_4^- in vitro requires stronger or more concentrated reducing agents than those likely to exist in the soil environment. Reduction of TcO_4^- by ferrous iron has been accomplished in the laboratory; however, it required $FeSO_4$ concentrations of the order of 10^{-4} M and elevated pH (8.5) (Lee and Bondietti, 1983).

The positive relationship between Tc sorption and soil water content results from the effect of the latter on the dissolved oxygen in the soil water and on the activity of the anaerobic microbial populations of the soil. As the soil water content increases, the diffusion of oxygen in the soil

water is reduced. The dissolved oxygen is consumed by aerobic bacteria and eventually depleted. As the partial pressure of O_2 in soil water decreases, the anaerobic and facultative anaerobic bacterial populations are favored. Some anaerobic and facultative anaerobic bacteria utilize nitrate, ferric and manganic oxides to dispose of the electrons generated in their catabolic oxidation of the organic material. These organisms are likely to reduce TcO_4^- in the same fashion. The hypothesis that TcO_4^- is used as electron acceptor in the respiratory chain of anaerobic bacteria has been discussed in Chapter III (pp. 42).

When both oxygen and nitrate have disappeared from the soil water, the soil redox potential drops to about -200 mV. Under these conditions, sulfate-reducing bacteria may develop and promote Tc complexation with organics or Tc precipitation as Tc-sulfide.

Anaerobic bacteria are not only present under flooded conditions. Even in well aerated soils, the presence of anaerobic centers inside the soil aggregates has been demonstrated (Sexstone et al., 1985). Therefore, the potential for a microbially-mediated reduction of Tc exists in these soils as well.

Once reduced, Tc complexes with the soil organic matter

$$TcO_4^- \xrightarrow{\text{anaerobic bacteria}} Tc(<VII) \xrightarrow{\text{soil organic matter}} TcOM$$

Technetium reduced by anaerobic bacteria to a state lower than VII complexes with the soil organic matter. The arguments supporting this statement are that (1) a reduced form of Tc (valence state lower than VII) is required for complexation to occur, and (2) up to 75% of the sorbed Tc is recovered by extraction of the soil organic matter. Furthermore, Tc-humic acids complexes have been synthesized *in vitro* by chemical reduction (Van Loon et al., 1986b).

As discussed in Chapter IV (pp. 72), Tc reactivity with the soil organics is directly proportional to the amount of functional groups (principally carboxylic) the latter carry. Consequently, Tc is predominantly associated with the low molecular weight organics of the

soil. Technetium sorption in soil can be equated to Tc complexation (chelation or covalent bonding) with the carboxyl groups of the soil organic matter.

In non-flooded soils, an equilibrium is established between reduction-complexation and oxidation of Tc

$$TcO_4^- < \underset{oxygen}{\underline{anaerobic\ bacteria}} > Tc(<VII) < \underset{oxygen}{\underline{soil\ organic\ matter}} > TcOM$$

Within the range of Tc concentrations used in this study, there was no limiting factor to Tc sorption in flooded soil; sorption was complete even at the highest Tc concentration (1.23 kBqmL^{-1} or 1.05 kBq g^{-1} soil). In contrast, when the soil was incubated at a lower water content, an equilibrium was established between Tc sorbed and TcO_4^- remaining in the soil water. The establishment of an equilibrium indicates that (1) availability of sorption sites for Tc sorption at field capacity is limiting, and/or (2) oxidation reactions competes with reduction-complexation reactions.

Since the "sorption sites" for reduced Tc are the reactive groups of the organic matter, flooding the soil do not create sorption sites, however, it could allow better contact between Tc and organic matter than in the case of soils at field capacity. The alternative explanation, schematized in the equation above, implies an equilibrium between reduction and oxidation of Tc. Pertechnetate is reduced by the anaerobic bacterial population of the soil, and the reduced forms of Tc (Tc(<VII), Tc-OM complexes) are oxidized in the presence of dissolved oxygen. As the water content of the soil increases, the equilibrium is driven towards sorbed Tc species because anaerobic bacteria are favored, and dissolved oxygen becomes limiting. The importance of the microbial activity in this process is emphasized by the fact that, in irradiated samples, TcO_4^- is favored.

Such equilibrium implies that the kinetics of oxidation of reduced Tc species compare with the kinetics of reduction of TcO_4^- by the bacteria. It was shown that upon drying the soil, some Tc-OM complexes oxidize quite

rapidly (see discussion pp. 75). Nothing is known about the kinetics of oxidation of the reduced species Tc(<VII) before they are stabilized by complexation with organics. Given the instability of these species in solution, it is reasonable to assume that their oxidation rate could be high.

Technetium equilibrium distribution in ApFC is a function of the initial Tc concentration in the soil water. This could be explained by a different concentration-dependence of the processes of Tc reduction (microbial) and Tc oxidation (chemical).

An alternative to reoxidation of reduced Tc species by oxygen is reoxidation mediated by bacteria. If the reduction of TcO_4^- is mediated by bacteria that reduce ferric and manganic oxides, the oxidation of reduced Tc could be mediated by bacteria that oxidize ferrous and manganous ions.

When the soil dries, Tc-organic matter complexes partially reoxidize and release Tc

Technetium desorption is a likely the result of the reoxidation of Tc-organic matter complexes, and takes place when the soil conditions are oxidizing (dry soil or fire).

In soils rich in organic matter, Tc behavior is dynamic and principally driven by the soil water content

As soil water content increases, sorption increases, and is maximum under flooded conditions. As the soil dries, the desorption process is maximized. In the field, soils are submitted to varying water inputs, a soil generally well aerated can remained waterlogged for a few days if a large rainfall or snowmelt takes place. These conditions may lead to an important sorption of Tc. Upon return to non-waterlogged conditions, or if a drought follows, Tc sorbed may partly return to solution. Such dynamic behavior makes difficult the assessment of Tc mobility and plant availability as a function of time in the short term. In the long term, unless waterlogged conditions are maintained, the dynamic behavior of Tc in conjunction with Tc leaching from the soil will eventually remobilize most of the Tc deposited.

B. Implications of Tc behavior in soil for radioprotection

Information on radionuclide behavior in the environment is gathered in order to assist decisions concerning (1) the acceptability of releases associated with the normal functioning of existing nuclear facilities, (2) the design and licensing of new facilities, (3) the emergency actions to take in case of accident to limit population exposure and radionuclide dispersion, and (4) the remedial actions to take in case of land contamination (e.g. leakage of disposed wastes, accidental releases). Some of these decisions are taken based on the results of risk assessments.

In radiological risk assessments, mathematical models are used to describe the distribution and transport of radionuclides in the environment and to calculate the doses to which humans are subjected by food and water consumption, or direct exposure. Many of these models are based on equilibrium distribution constants (termed distribution coefficients and transfer factors) between soil/water, plant/soil, milk/vegetation, and meat&eggs/vegetation.

The soil to water concentration ratio, or soil to water distribution coefficient, or Kd (mL/g), relates the equilibrium concentration of radionuclide in the soil (Bq/g) to its equilibrium concentration in the equilibrating water (Bq/mL). A large Kd value indicates that the radionuclide is preferentially associated with the soil, whereas a Kd of 0 indicates no radionuclide association with the soil. The most common technique used to determine Kd is by short-term batch equilibrium techniques.

The Kd values used in existing radiological assessment models for Tc are "default" values, chosen before data on Tc behavior in soil were available; they are documented in Till et al. (1980). The CRRIS model uses a Kd value of 1.5, whereas the USNRC in Regulatory Guide 1.109 makes the assumption that no Tc is removed from the soil layer in 15 years, i.e., that Kd is infinite in that time. The use of an elevated Kd in radiological assessment models is conservative (i.e., overestimates the risk) because it implies that Tc remains in the soil. Since the amount of Tc in vegetation is calculated from the amount of Tc associated with the soil via the plant/soil transfer factor, an

elevated Kd maximize the amount of Tc accumulated in plant material. At the time it was made (1977), this assumption was acceptable because the chemical form of Tc associated with the soil was unknown. However, recent research on the uptake of Tc by plants (Van Loon, 1986a) has shown that the sole bioavailable form of Tc is TcO_4^- present in the soil water; i. e., Tc sorbed in the soil is not readily available for plant uptake. Therefore, in soils that strongly sorb Tc (have a elevated Kd), plant uptake will be reduced. It is clear that the use Kd, in its present form, is confusing and misleading.

Furthermore, in recent years, conservative assumptions in risk assessments and the use of Kd in general have received strong criticisms. First, the radiological protection standards of maximum permissible dose to the whole body of a member of the general public were lowered from 500mrem to 25mrem (Hoffman and Gardner, 1983), and conservatism in dose calculation no longer produced estimates that could be considered well under the permissible dose. Second, radioprotection and waste management programs changed their emphasis from conservative assessment models to models that predict as accurately as possible environmental exposures and eventual human doses. Furthermore, sufficient data were accumulated on the behavior of radionuclides to lead experimentalists to consider that a single parameter (Kd) and equilibrium models were not acceptable descriptions of the interactions of radionuclides with soil (Sibley and Myttenaere, 1986). It was suggested that Kd be replaced by a soil-submodel.

The most important impediment to a detailed soil-submodel which takes into account the real-world processes is the limited information on the environmental system that is available to the individual performing the risk assessment. Furthermore, the cost of producing a sophisticated model is worthwhile only if there is assurance that its predictions are more accurate than those of a less elaborate model. If a stable isotope or stable analog element is known for the radionuclide under study, its long-term distribution in the geosphere can be modeled after that of the stable species. If no stable analog is known (which is the case for Tc), the key to a simple but meaningful soil-submodel is (1) to reach an understanding of the processes

governing its behavior in soil and (2) use this understanding to carefully select a few critical parameters among the factors affecting the processes.

The number of parameters that can be used in any model is limited by the amount of information available on the environment in which the radionuclide is released. Site-specific models can be developed using measured properties of the site, and therefore can be more elaborate than generic models. The known factors and processes affecting Tc behavior in soil are discussed below in terms of directions and recommendations for a modelling effort.

The framework of a soil-submodel is provided in Fig. V.1. Pertechnetate input is subjected to simultaneous leaching, plant uptake, and sorption in soil. Sorption is partially reversible by oxidation of the soil organic matter-Tc complexes. Technetium bioaccumulated in plant material that is not harvested returns to the soil system partly as TcO_4^- (C. Myttenaere, personal

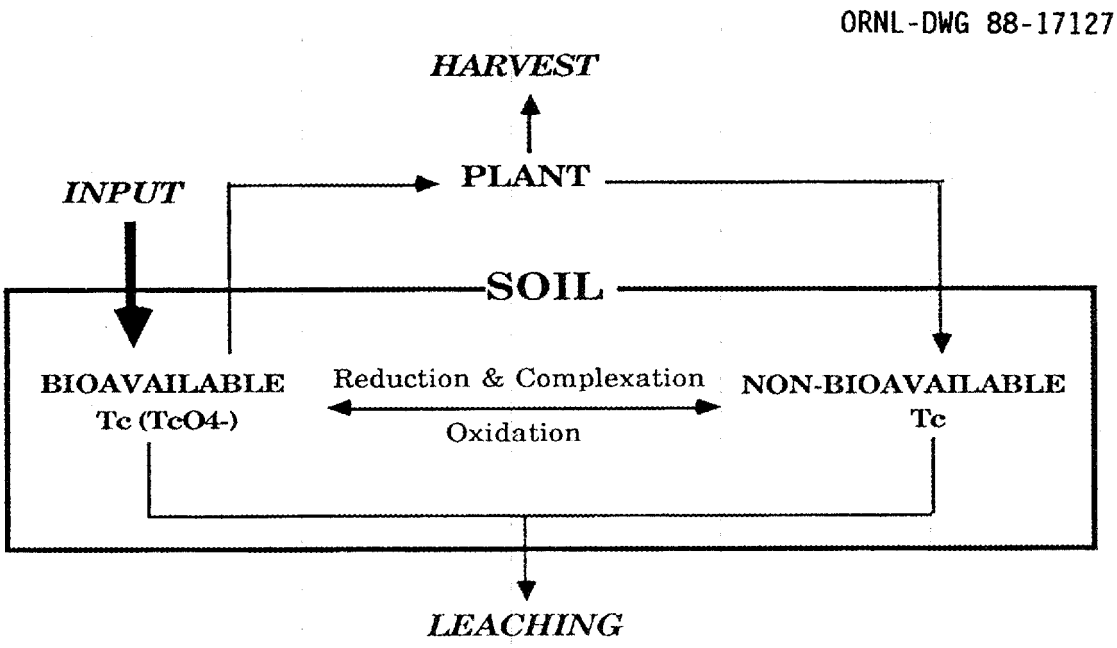

Fig. V.1. Framework for a model of Tc behavior in soil.

communication) and partly as non-bioavailable Tc. Both plant harvest (for direct human consumption or for animal forage) and Tc leaching to the drinking water supplies contribute to human exposure.

Importance of soil type

This study and literature data suggest that the single most important predictive parameter of the extent of Tc sorption is soil type, more specifically, soil organic matter content. Soils that do not contain enough organic matter to support a high microbial population sorb little Tc whereas soils richer in organic matter have higher potential to sorb Tc.

In absence of better estimate of Tc sorption, the simplest meaningful variation to the existing Kd is to assume a Kd of 0 (no sorption) for soils in which organic matter content is lower than a certain breakpoint value, and to use a Kd function of environmental parameters for soils with organic matter content higher than the breakpoint value. This breakpoint value could be determined by incubating ***fresh*** soil samples of different organic matter contents under flooded conditions until equilibrium is achieved. (Sorption is maximized under flooded conditions *if* the bacterial population is intact). In the absence of such data, a breakpoint of 0.2% (the organic matter content of the Bt soil used in this study) could be used since negligible sorption was observed in this soil.

Based on the belief of high Tc geomobility, the use of a Kd of 0 across soil types has been suggested. It is apparent that this assumption would not be accurate; most agricultural and forest soils have a developed A horizon (rich in organic matter) in which Tc sorption would take place. In field experiments, Tc is found to be concentrated in the first few centimeters of the soil profile (Hoffman, 1982a,b; Garten et al., 1984). Furthermore, this assumption would not necessarily be conservative (i.e., maximize plant uptake and dose to humans). Sorbed Tc can be partially remobilized, therefore, assuming that all Tc is immediately available for plant uptake and leaching can underestimate the plant uptake that would occur if Tc is sorbed and remobilized as a function of

variation in environmental conditions.

There is no single parameter that can characterize Tc sorption across soil type; Kd can be expected to vary from 0 to infinity (all Tc sorbed) as a function of soil type and environmental conditions. Therefore, taking the mean and variance of all Kd reported in the literature to use in assessment models would only reflect the type of soils and experimental conditions the researchers used, and not the intrinsic variability of the parameter.

Environmental parameters

Based on the conceptual model of Tc behavior in soil, the 2 environmental parameters critical for Tc sorption would be (1) the anaerobic microbial activity of the soil and (2) the soil water status and its fluctuations. (A rewording of these 2 parameters into "soil redox conditions" would not be as accurate because it would de-emphasize the biological aspect of the process and therefore lead to an underestimate of the effect of environmental factors like temperature.) As illustrated in Fig. V.2, soil organic matter content, anaerobic microbial activity, and soil water content are interrelated, and the 2 latter factors are themselves a function of soil structure and climatic variations in temperature and rainfall.

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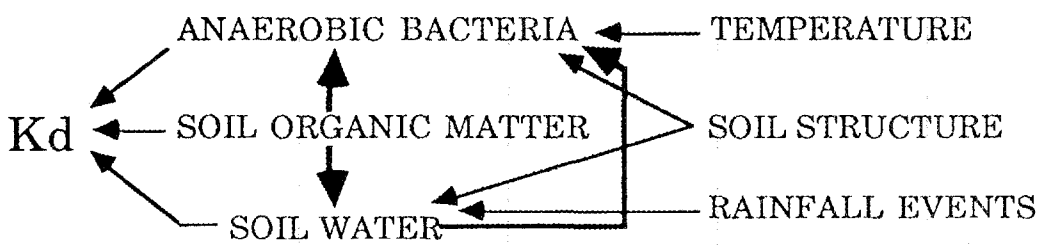

Fig. V.2. Environmental factors governing Tc sorption.

The role of rainfall intensity and temperature as driving environmental parameters for Tc sorption in soils for which Kd is not 0 should be validated by field experiments. Soil structure is important for both Tc leaching and sorption; poorly structured soils are poorly drained and may develop prolonged anaerobic conditions.

In agroecosystems, farming practices could have an important impact on Tc sorption. Tillage and compaction have a negative effect on the soil structure, and promote anaerobic conditions. Application of farm manure (readily decomposable material) favors the development of an active anaerobic population.

Effect of Tc input

In Ap (soil horizon for which Kd was not 0), as Tc input to the soil increased, Kd decreased, except under flooded conditions where, in the range of the experimental concentrations, sorption was complete. This suggests that the effect of the initial Tc concentration in the soil water on Kd is less important than the effect of the soil water content.

For detailed site-specific models, Freundlich isotherms encompassing the array of expected Tc inputs can be obtained by using the soils present on the site and the methodology described in this study.

Remobilization of Tc

This study and that of Stalmans (1986) have shown that Tc is immobilized principally by complexation with the soil organic matter. However, this Tc sink is temporary; Tc immobilization is maintained as long as the conditions favorable for sorption persist, and an important remobilization can take place when the soil is subjected to periods of drought. On an annual scale, Tc remobilization would be driven by seasonal modifications of the soil water content. In the long-term, Tc-organic matter complexes will be subjected to microbial decomposition.

Furthermore, in natural systems, Tc taken up by plants eventually returns to the soil under TcO_4^- and under non-bioavailable form. Garten and

coworkers (1986a) have shown that, in a Tc-contaminated woodland ecosystem, even though the major Tc sink was the soil, Tc was accumulated in large quantity in herbaceous plants and tree leaves. However, trees themselves represented the major above-ground Tc pool. Therefore, decay of leaf litter and annual plants, and tree fall constitute secondary sources of Tc even after the primary input is discontinued. Bioincorporated Tc is in large part associated with organic components (Garten et al., 1986b; Garten and Lomax, 1987; Lembrechts and Desmet, 1986; Lembrechts et al, 1985; Cataldo et al., 1986). Data on the mineralization rate of Tc from leaf litter and woody biomass are needed to estimate the return of bioincorporated Tc to the plant-bioavailable Tc pool (TcO_4^-).

In consequence, the 2 secondary sources of Tc over time, reoxidation of Tc sorbed in the soil and mineralization of Tc accumulated in the plant biomass, are important for accurate long-term assessment of Tc behavior in the environment and should not be overlooked.

Dynamics of Tc in soil

Kinetics of both sorption and desorption processes observed in this study are rapid. Equilibrium is achieved in a matter of days and persists if not disturbed by a modification of the soil water content. Based on these rapid kinetics, it can be assumed, to simplify the problem, that (1) the equilibrium distribution of Tc in soil is achieved instantaneously as the environmental conditions are modified, and (2) the dynamic of Tc in soil is ruled by the variation in soil water content rather than by time.

Other authors observed a substantially slower desorption kinetic, characterized by half-life values of 46 (Bondietti and Garten, 1986), and 7, 114, and 120 days (Stalmans, 1986). As discussed on pp. 76-77, the reasons for the differences in oxidation rate are not entirely clear. The approach taken in this study is closer to field conditions, thus extrapolation of observed rates to Tc behavior in the environment is more valid. However, if concensus is not achieved, more research is necessary to determine which Tc desorption rate is more appropriate to use for risk assessment. If the desorption kinetic is

indeed slower than observed in this study, Tc desorption as a function of time should be considered as well.

Conclusions

This study and available literature data suggest that soil parameters such as soil organic matter content and soil structure, and climatic parameters such as temperature and rainfall events could be used as indicators of Tc behavior in soil. However, field studies are necessary to verify the role of these parameters in governing Tc mobility in soil. If the discussion presented here is validated by field observations, a Kd of 0 could be attributed to soil with an organic matter content lower than a given value (0.2% is suggested). For soil with organic matter content higher than this value, Kd could be a dynamic parameter governed by the fluctuations of soil water content and temperature rather than by time. Wet periods promote Tc sorption and dry periods remobilization of sorbed Tc. In long-term models of Tc distribution in soil, secondary sources of Tc (reoxidation of sorbed Tc and mineralization of bioaccumulated Tc) should also be considered.

The relevance of parameters of radionuclides behavior determined in temperate climates for risk assessment in tropical countries with a developing nuclear energy (e.g. Brazil) is a subject of concern. A model of Tc behavior developed from soil organic matter content and climatic properties could be inapplicable for the tropics; some tropical soils (Oxisols) have a subsurface horizon dominated by Fe and Al oxides. In these soils, Tc sorption process could be governed by anion exchange rather than complexation with organic material. A reevaluation of the model structure is necessary before its application in tropical parts of the world.

For detailed site-specific models, it is worthwhile to measure sorption potentials on soils present in the site. Such information can be obtained at a minimal cost by using the method developed in this study to measure Tc sorption in soil. The method is inexpensive, nearly as simple as the batch equilibrium technique, yet more representative of field conditions.

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APPENDIX

Unit Conversion Table for the Isotope 99 of Technetium

Bq	Ci	mole
37 milli	1 pico (p)	0.6 pico
37	1 nano (n)	0.6 nano
37 kilo (k)	1 micro (μ)	0.6 micro
37 mega (M)	1 milli (m)	0.6 milli
37 giga (G)	1	0.6
37 tera (T)	1 kilo	0.6 kilo

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