ACKNOWLEDGEMENTS

Special recognition is given to Kathy Gallagher and Peter Holmberg, who have made valuable contributions to the project while serving in the role of Laboratory Technicians.

LEGAL NOTICE

ABSTRACT

Studies described in this report were aimed at establishing the magnitude and mechanisms of ^{99}Tc sorption by soils and uptake by plants. Results show that ^{99}Tc was sorbed from solution over a period of two to five weeks by 8 of 11 soils studied. The slow rate of sorption, the lack of sorption by low organic matter soils, the elimination of sorption following sterilization and increased sorption following addition of dextrose all point to a microbial role in the sorption process. However, it has not been established whether this is a direct or indirect role nor is it possible to clearly predict the conditions under which sorption will occur. Results of plant uptake studies show that ^{99}Tc can be taken up and translocated into the photosynthetic tissue of higher plants with concentrations in seeds being much less than in vegetative tissue. Technetium-99 was also shown to be toxic to plants at low concentrations and evidence suggests that this is a chemically rather than radiologically induced toxicity. However, this remains to be completely resolved as well as whether there is a threshold level of ^{99}Tc required before toxicity occurs. Studies of short-term, dynamic, aerobic systems indicated that ^{99}Tc moves through the soil as a relatively large anion exhibiting characteristic miscible displacement with some asymmetric tailing. ^{99}Tc exhibits greater retention that Cl^-, which may be attributed statistically to weak complexion by organic matter. It is unlikely that this retention phenomenon is related to the static sorption activity reported in the first part of this study.

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INTRODUCTION

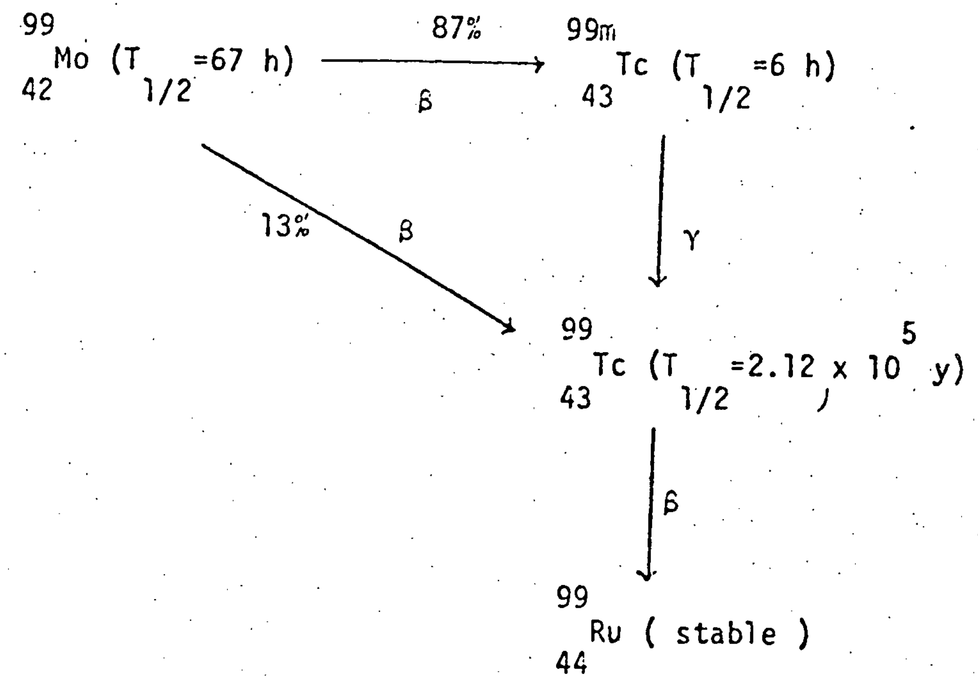
This technical progress report covers the results of studies dealing with the behavior of technetium-99 in soils and plants for the four year period from April 1, 1974 to December 31, 1978 under contract number EY-76-5-02-2447.M002 with the U.S. Energy Research and Development Administration. Approximately 10 percent of the principal investigator's time was devoted to the project during the reporting period.

Many of the results presented in this report have been reported in earlier progress reports (U.S. ERDA No.'s COO-2447-1, COO-2447-4, or COO-2447-5) or in the manuscripts listed in the Literature Cited section which have been submitted and approved for publication (Landa et al., 1976; Gast et al., 1976; Landa et al., 1977). They are presented in total here in order to tie them together in one central, coherent report.

REVIEW OF LITERATURE AND STATEMENT OF PROBLEM

An examination of the mass yield curves for the fast neutron fission of ^{238}U, ^{239}Pu, and ^{232}Th and the slow neutron fission of ^{233}U, ^{235}U, and ^{239}Pu reveals maximum yields at mass-99. This leads to the production of element 43, technetium, as shown by the following decay scheme.

DECAY SCHEME: MASS 99 CHAIN



Technetium is a transition metal of group VII B, and its isotopes, ranging in mass number from 92 to 107, are all radioactive. Of these, only ^{99}Tc is a long-lived ($T_{1/2}$ = 2.12 x 10^5 y) fission product, emitting a 0.292 Mev (max.) beta particle (U.S.P.H., 1970).

Technetium-99 may enter the environment from several sources. That found in rainwater is believed to result from atmospheric detonations (Attrep *et al.*, 1971). Leaky fuel elements in nuclear reactors, losses during fuel reprocessing, neutron activation of Mo in coolant waters, fuel claddings, and reactor construction materials represent additional methods of ^{99}Tc production and release to the environment. Indeed, ^{99}Mo, ^{99m}Tc and ^{99}Tc are often reported in reactor effluents (E.P.A., 1971; Toyota et al., 1971).

In addition, ^{99}Tc and its mass 99 parents, isolated from either neutron-activated molybdenum or mixed fission product waste solutions, are finding increased medical and industrial applications. The widespread use of ^{99m}Tc in nuclear medicine for diagnostic organ scanning, and its subsequent elimination in patients' excretions provide an additional source of ^{99}Tc to the environment. Small quantities of Tc have been shown to impart remarkable corrosion resistance to soft metals (Colton, 1965) and if the alloying of such steels with ^{99}Tc becomes an accepted practice, still another route of release will be introduced. The trace amounts of naturally-occuring ^{99}Tc associated with uranium ores (Kenna, 1962) and ^{99}Tc produced as a result of high-energy spallation reactions (Goeckermann and Perlman, 1949) probably contribute only very slightly to environmental levels.

Thus several important sources of ^{99}Tc release to the environment presently exist, and with the growing development of nuclear power reactors, and of medical and industrial utilization of ^{99}Tc and its mass-99 parents, it appears that such release will continue. These releases of technetium will generally be as the pertechnetate ion, TcO_4^-. Although Tc may exhibit a valency from 0 to 7, with 4+ and 7+ being the most common, the TcO_4^- ion is the only species which has been found in aqueous solution over a wide pH range (Rulfs et al., 1967). Also, this is the chemical form utilized in nuclear medicine (Harper, 1964) and industrial applications (Colton, 1965), and the final form in which Tc occurs following the radiochemical reprocessing of spent reactor fuel elements (Parker et al., 1956).

Considerable work has been done on the movement of administered Tc in laboratory animals and humans. Following uptake, the Tc tends to concentrate in the thyroid and salivary glands, and the gastric and nasal mucosa (Baumann et al., 1956; Beasley et al., 1966). The movement and degree of concentration of Tc appears similar to that of iodine, and indeed hyperthyroid individuals show a much greater localization of administered Tc in the thyroid as compared with normal individuals (McGill et al., 1971). Elimination is initially by the urine, and after several days, predominantly the feces (Beasley et al., 1966; Sorensen and Archambault, 1963). While most studies have involved the intravenous administration of Tc, the work of Beasley and coworkers (1966) showed no detectable difference in the rate, route or amount of excretion in human volunteers given Tc by either injection or ingestion, the latter probably being the major route of exposure to environmental levels of Tc. An autopsy study (Sodd and Jacobs, 1968) of environmentally - exposed individuals revealed small but detectable amounts of ^{99}Tc deposited in hyman thyroid glands.

In contrast to the relatively extensive studies of Tc in animals and humans, there was little direct information available concerning its behavior in soils at the time this study was initiated. However, the medical and analytical chemistry literature does suggest a variety of mechanisms by which technetium may react with the organic and mineral components of natural soil systems. These mechanisms, which have been reported for technetium in non-soil systems, include ion-exchange, precipitation/coprecipitation and complexation/chelation. For example, Linder (1965) has demonstrated the non-specific anion exchange adsorption of the pertechnetate anion at the amphoteric surface of pseudomorphic iron hydroxide. This appeared to be a potentially important mechanism for technetium retention in soils, for as Ryabchikov and Pozdnyakov (1965) have shown for anion exchange resins, the small hydration of the TcO_4^- ion results in marked preferential adsorption of trace quantities even from solutions of very high ionic strength. Since there are no stable isotopes of technetium, the TcO_4^- will be carrier free, and the quantities present will be very small. Consequently, even the relatively small anion exchange capacity of montmorillonitic and kaolinitic type minerals appeared to be adequate for retention.

The pertechnetate anion also forms slightly soluble salts with a variety of inorganic cations, and consequently may be retained by this mechanism in those soils with high concentration of free iron, aluminum and silica. In addition, it may coprecipitate with various metallic sulfides. However, it does not coprecipitate with ferric hydroxide unless reduced to the 4+ oxidation state (Anders, 1960).

Chelation also appears to be a feasible mechanism for technetium retention by soils in light of its electronic structure (available "d" orbitals for bonding), and the observation that the extraction of the pertechnetate ion from mixed fission products requires the presence of an electron donating nitrogen or oxygen atom in the solvent (Peacock, 1966). Also, a variety of biomedical products consist of complexes of ^{99}Tc with amino acids, proteins, or polyaminecarboxylic acid (i.e. EDTA-type) chelating agents. It is a matter of current controversy, however, as to whether the Tc is present as pertechnetate or as a reduced, cationic species in such complexes (Benjamin *et al*., 1970; Eckelman *et al*., 1971).

The limited information available in the literature concerning the rates of movement of Tc in soils was inconclusive. Brown (1967) reported that ^{3}H, ^{106}Ru and ^{99}Tc have poor sorption properties and migrate at approximately the same rate as the groundwater. This observation was based on studies involving the discharge into the ground of waste solutions from the U.S. Atomic Energy Commission's Chemical Separations Plants at Hanford, Washington. In contrast, Handley and Babcock (1970, 1972) have shown that ^{106}Ru is held very tightly at the surface of soil colloids. Further work done at the Georgia Institute of Technology on a simulated aquifer (Champlin, 1967) suggests that the anomalous mobility of ruthenium observed at the Hanford waste disposal site may be due to its movement as an adsorbed phase on micron-size particulate matter. This possibility has not been investigated in the case of ^{99}Tc.

The results of several investigations relevant to the environmental release and fate of ^{99}Tc have been reported since initiation of the study reported here. Moss and Sternglass (1973), in a study of radionuclide releases to the Ohio River associated with the operation of the nuclear medicine departments of twenty-one Pittsburg hospitals, found ^{99m}Tc to be the second largest contributor of activity from these sources. Based on the period 1969-1971, they calculate a ten-to-fifteen percent annual increase in total radioisotope usage. Thus, as ^{99m}Tc continues to gain in popularity as the radionuclide of choice in many diagnostic procedures, its usage and, hence release to the environment, will undoubtedly outstrip the increase in total medical radionuclide usage.

Reports by the U.S. Environmental Protection Agency (1973) and the U.S. Atomic Energy Commission (1974) on the uranium fuel cycle have provided estimates of the growth of the nuclear electric generation capability in the United States. In 1972, an estimated 10,000-12,000 megawatt electrical (MWe) of nuclear electric generation capability is predicted to have expanded to 140,000-150,000 MWe (U.S. Atomic Energy Commission, 1974). Kotegov et al. (1968) have provided the following equation relating the quantity of technetium formed to the reactor power: $N_{Tc} = 28\ Pt$

where N_{Tc} = amount of Tc formed, mg.

P = reactor power, MW

t = time of operation of the reactor, days.

Based on the above data, an estimated 1500 kg of Tc will be formed in the year 1980 by nuclear power generation in the United States. Kotegov et al. (1968) also estimated the world-wide production of technetium from nuclear power generation to be 4000 kg for the year 1980, and based on the period 1963 to 1970, estimated the accumulated quantity of technetium to be in excess of 10,000 kg.

Gearing et al. (1973) have investigated possible toxicity levels of ^{99}Tc (as the pertechnetate ion) for several marine and freshwater blue-green algae. They found no significant concentration of ^{99}Tc in the cells at rather high concentrations of NH_4TcO_4 (7.56×10^{-4} $\underline{M}$).

Two recent investigations have been concerned with determining trace amounts of ^{99}Tc in environmental samples. Foti et al. (1972) have developed an extraction-neutron activation technique for use in detecting ^{99}Tc in vegetation samples. Golchert and Sedlet (1969) have reported a chemical separation technique which has been used to detect ^{99}Tc in surface water samples. Of some 150 water samples analyzed during the period 1965-1968, 80 percent fell below the detection limits of the procedure (0.5 pCi/l). The average concentration in the remaining 20 percent was 4.65 pCi ^{99}Tc/l.

A recent report from Battelle Pacific Northwest Laboratories (Wildung, R.E. et al., 1974) on pertechnetate sorption from 0.01 $\underline{M}$ $CaCl_2$ by a variety of soils indicates only limited removal of technetium from solution. However equilibration times were only 22-24 hours, in contrast to the extended time periods found in our investigations to be necessary to achieve equilibrium conditions. In addition, Cataldo et al. (1978) have recently reported on the accumulation, fate and behavior of technetium in plants. Like many of the results reported here, they found that ^{99}Tc is effectively accumulated by plants, that Tc is toxic to plants at low concentrations apparently due to chemical rather than radiation effects, and that the xylem form of Tc was TcO_4^-.

In light of the projected increases in ^{99}Tc release to the environment outlined above, the rates and mechanisms of its incorporation into the food chain need to be understood as well as the radiological health implications. However, information concerning the behavior of technetium in soil systems and its availability for plant uptake were almost nonexistent at the time this study was initiated. It seemed appropriate then that a comprehensive study be conducted to establish its general retention by soils, the extent that it may be taken up by plants and incorporated into the food chain, and the movement of ^{99}Tc in soils.

MATERIALS AND METHODS

Technetium-99 source:

Technetium-99 was obtained from the International Chemical and Nuclear Corp., Irvine, California. The carrier-free material is supplied in 1 N NH_4OH in the form of ammonium pertechnetate (NH_4TcO_4).

Radioassay for ^{99}Tc:

Technetium-99 was determined using a Packard Tri-Carb liquid scintillation spectrometer (model 3375) with the discriminators and amplification preset for ^{14}C counting. The basic scintillant used consists of:

5.5g PPO (2,5 Diphenyloxazole)
0.1g Dimethyl POPOP (1,4 - bis - 2 - (4-Methyl - 5 Phenyloxazolyl)-Benzene)
667 ml Toluene
333 ml Triton X-100

The scintillators and Triton X - 100 were scintillation grade materials and the toluene was A.C.S. analytical reagent grade. A variant of this formulation containing no secondary scintillator was used with samples containing perchloric acid. Low-potassium borosilicate glass vials were used and counting efficiencies ranged from about 80 to 90%. Quench corrections were made using the external standard method. Samples were counted for 10,000 net counts or 20 minutes.

Ashing of plant samples:

In order to prevent the volatile loss of technetium, the acidic dissolution of samples must be conducted under refluxing and strongly oxidizing conditions (Anders, 1960). Based on these guidelines, the work reported by Sodd and Jacobs (1968) on ashing human thyroid tissue, and the acid co-distillation data of Boyd et al. (1960), a suitable procedure compatable with the analysis of a relatively large number of plant tissue samples by liquid scintillation techniques was sought. A modification of the method of Mahin and Lofberg (1966) was found to offer both ease of sample preparation and freedom from the volatile loss of technetium.

Five to 10 mg samples of plant tissue, ground to pass the 20-mesh sieve of a Wiley mill, were placed in a tared glass scintillation vial and 0.2 ml 60% perchloric acid and 0.4 ml 30% hydrogen peroxide added. The vials were sealed with linerless polyethylene screw caps and digested in an 80°C oven for 16 hours without agitation. After cooling, 10 ml of the modified (no dimethyl POPOP) scintillant was added to each vial. The vials were shaken, cooled for 1 hour in the sample compartment of the liquid scintillation unit, and then counted.

Soil characterization:

Soils for this study were selected to reflect the general range of pH, organic matter content, and texture found in the state of Minnesota. Mineral soil samples were collected in the field, air-dried, ground and passed through a 2 mm sieve. The organic soil studied was maintained in the field moist state without grinding.

The following soil characteristics were determined on duplicate samples using the methods cited.

a) Particle size distribution was determined by the hydrometer method of Day (1965) as modified by Grigal (1973).

b) Specific surface area of the mineral fraction of the soil was determined by the ethylene glycol monoethyl ether method of Heilman *et al*. (1965) as modified by Eltantawy and Arnold (1973).

c) Moisture retention was determined at 1/3 - and 15-bar matric suction on a pressure-plate apparatus using the method of Richards (1965).

d) The pH of 1:2.5 soil:water and soil: 1 *N* KCl slurries was determined using a Beckman Research pH meter with glass electrode as described by Jackson (1967).

e) Organic carbon was determined by the Walkley-Black wet combustion method as described by Allison (1965).

f) Calcium carbonate equivalent was determined by the acid neutralization method as described by Allison and Moodie (1965).

g) Free iron oxides were determined by the sodium dithionite method of Deb (1950) as modified by Kilmer (1960).

h) Cation exchange capacity was determined by a modification of the radiometric method of Francis and Grigal (1971) using 0.1 N CsCl labeled with ^{137}Cs as the saturating salt.

i) Extractable phosphorus was determined using Bray's No. 1 extractant according to Grava (1968).

j) Exchangeable potassium was determined by ammonium acetate extraction according to Grava (1968).

Sorption of ^{99}Tc by soils:

General procedure: All soil sorption experiments involved the following general procedure. Two grams of air-dry soil, ground to less than 60 mesh, were placed into sections of seamless cellulose dialysis tubing (Union Carbide Corp., Food Products Div., Chicago, Illinois) which had been previously washed in 0.05 N HCl and deionized water, knotted on one end and opened with an air stream. Ten milliliters of distilled water was added to each bag and the open end of the bag was sealed with a knot. The bags were than placed in 60 ml linear polyethylene bottles (Nalgene Labware; Nalge Co., Rochester, N.Y.), and 25 ml of ^{99}Tc bearing aqueous solution added. The bottles were sealed with polypropylene screw caps and the neck of the bottle covered with adhesive tape to prevent evaporation. Preliminary experiments showed no adsorption of ^{99}Tc from solution by the polyethylene bottles or dialysis tubing in the absence of the soil, and that equilibrium with respect to ^{99}Tc concentration was established across the dialysis bag (average pore size of tubing, 24 Å) within 7 hours at 25°C. The samples and controls were placed in a 25°C water bath and 1 ml aliquots of the solution outside of the bag were taken at given time intervals to establish the extent of sorption by the soil. Once sampled (3 - 1 ml aliquots per bottle; 2 bottles per soil per sampling time) the bottles were removed from the study (due to changed soil/solution ratio). The fraction, (C/Co), of the ^{99}Tc concentration remaining in solution at a given sampling time, (C), to that in the control solutions, (C_0), was determined and plotted as a function of time.

Preliminary soil sorption experiments: Preliminary experiments were conducted to determine the general kinetics and extent of ^{99}Tc sorption by several of the test soils. The general procedure outlined above was followed except that the experiment was run at ambient temperature (25-32°C) and samples were not replicated. In addition, sorption of ^{99}Tc from solution in a well mixed aqueous soil suspension without the dialysis bag was determined to establish whether diffusion of ^{99}Tc within the bag-enclosed soil mass was a rate limiting step. Four hundred and fifty ml of suspension having the same amounts of soil, water, and ^{99}Tc as in the regular experiments was prepared. The suspension was mixed continuously at 25°C for two days. After this time, the suspension was placed in the 25°C water bath and shaken vigorously once a day for the duration of the experiment. At given time intervals, 3 ml aliquots of the suspension were removed, centrifuged and filtered through Whatman #42 filter paper (shown not to adsorb Tc). Two 1 ml aliquots of the filtrate were counted in 10 ml of the liquid scintillation formulation as described in the radioassay section and the amount of sorption compared to that in the presence of the dialysis bag.

Sorption of ^{99}Tc by whole soils: Having established the approximate time required to achieve equilibrium in the preliminary experiments, a replicate study of similar design was set up to determine the extent of ^{99}Tc sorption by 11 Minnesota soils from aqueous solutions at 25°C.

Separate bottles containing the ^{99}Tc solution plus soil in dialysis tubing were set up for sampling at each time period. Samples were equilibrated for 2 to 3 weeks before initial sampling, and then sampled at given intervals thereafter.

Effect of selective dissolution treatments on sorption of ^{99}Tc: Early results showed that the Zimmerman surface soil and the Nicollet subsurface soil exhibited little or no sorption of ^{99}Tc. The most obvious property shared by these soils is a low organic matter content. Therefore, it was decided to determine sorption by the previously high sorbing, high organic matter Bergland soil following extraction of the organic matter by hydrogen peroxide digestion. Ten gram samples of air-dry soil, ground to pass a 2 mm sieve, were digested at 75^{0}C over a 7 day period with 385 ml of 30% H_2O_2. The digestion beakers were then placed in a 105^{0}C forced draft oven for destruction of remaining peroxide and residue drying. The dried mineral material was ground with an agate mortar and pestle to pass a 60-mesh (250 micron) sieve for use in the organic matter-free sorption studies.

As the Bergland soil is also high in free iron oxides, a species shown by other workers in non-soil systems to sorb the pertechnetate ion (Linder, L., 1965), selective removal of these materials was performed following the method of Kilmer (1960). Eight gram samples of air-dry, 2 mm Bergland soil plus 8.0 g of sodium dithionite and 150 ml of deionized water were added to 250 ml polyethylene bottles and shaken for 17 hours. The suspension was acidified with 10% HCl to pH 4.0 in order to destroy any ferrous sulfides that may have formed, and then centrifuged. The supernatant was decanted and the soil washed with 200 ml of deionized water by centrifugation 3 times. This washed soil was transferred to dialysis tubing and washed 3 times against 20 liters of deionized water resulting in a Cl^- free dialysate as tested by 1% $AgNO_3$. The soil was dialysis-washed twice more and then dried at 105^{0}C. The residue was ground with an agate mortar and pestle to pass a 60-mesh sieve and used in sorption studies.

Effect of increasing ^{99}Tc levels on sorption by soils: The levels of ^{99}Tc used in the previous experiments were arbitrarily selected at about 30 nCi/g of oven-dry soil. In order to see how this quantity might compare to the total sorption capacity of the soil, ^{99}Tc concentrations of about one and two orders of magnitude greater were studied in otherwise identical distilled water - sorption systems.

Effect of KCl and KH_2PO_4 on ^{99}Tc sorption by soils: Anion exchange is one possible mechanism of ^{99}Tc sorption, especially from aqueous solutions low in other free electrolytes. To determine whether this mechanism is responsible for previously observed results, sorption of trace quantities of ^{99}Tc by Arveson and Bergland soils was determined in the presence of 0.1 N aqueous solutions of KCl and KH_2PO_4. Phosphate was selected to check for the inhibition of sorption due to the blockage of specific adsorption sites (such as exist for phosphate adsorption on ferric oxide surfaces).

Based on electrical conductivity measurements, the soluble salt levels initially present in the experimental systems correspond to Cl^- concentrations (as NaCl) of 0.0054 and 0.00046 N for the Arveson and Bergland, respectively. Hence, the KCl additions represent a minimum of 13- and 150-fold increases in the Cl^- level of the Arveson and Bergland systems, respectively.

The Arveson and Bergland soils initially contained 4 and 10 ppm extractable P, respectively as determined by Bray's No. 1 solution. Using surface areas of 99 and 220 m^2/g soil measured for the Arveson and Bergland soils, respectively by the method of Eltantawy and Arnold (1973), and the phosphorus adsorption maxima relationships developed by Olsen and Watanabe (1957) for alkaline and acid soils, we calculate adsorption maxima of 12 and 50 mg P/100g soil for the Arveson and Bergland, respectively. Hence, the P initially present in the Arveson represents about 3% of the adsorption maxima, while the added P represents about 320 times that required for saturation of the P-sorption sites. For the Bergland, that P initially present represents about 2% of the maxima, and the P added represents about 80 times that required for saturation.

Extraction of sorbed ^{99}Tc from soils: Many of the above sorption experiments demonstrated the disappearance of ^{99}Tc from solution. It remained necessary however to establish that this disappearance was due to sorption by the soil rather than loss by volatilization. Since it is difficult to count the ^{99}Tc on the soil directly, the following ^{99}Tc extraction experiments were conducted to both establish the presence of the ^{99}Tc on the soil and the relative effectiveness of the different extracting agents.

Two grams of air-dry soil (Bergland and Arveson) were placed in a tared 50 ml polypropylene centrifuge tube with screw closure (Nalgene Oak-Ridge type) along with 25 ml of distilled water containing 0.06 µCi of ^{99}Tc. The tubes were sealed and placed in a 25^{0}C water bath. After one month the tubes were removed from the bath and centrifuged for ten minutes at 15,000 RPM. The supernatant solution was filtered through Whatman #42 filter paper and aliquots taken for counting. The solution was in all cases found to contain less than 2% of its initial ^{99}Tc activity.

Based on preliminary trials of different extractants, 1.0 N solutions of perchloric acid and sodium hydroxide were chosen for study. Twenty five milliliters of each extractant were added to duplicate samples of each soil. The tubes were sealed, the soil dispersed using a Vortex-Genie, and then placed horizontally and shaken for 24 hours at room temperature. The tubes were then centrifuged and filtered as above. The extraction procedure was repeated 4 times.

The initial NaOH extracts were very dark colored, presumably due to organic matter. The $HClO_4:H_2O_2$ wet ashing procedure (Materials and Methods: ashing of plant samples) was attempted in an effort to both neutralize and clarify these extracts. The attempt however, proved unsuccessful yielding a gummy, dark brown residue. It was, therefore, necessary to dilute the initial NaOH extracts 10-fold in volumetric flasks. One milliliter aliquots of the diluted NaOH extracts were then placed in glass scintillation vials and taken to dryness in an 80°C oven. The residue was then wet-ashed using the $HClO_4$:H_2O_2 procedure, yielding a colorless solution which was subsequently counted. The succeeding NaOH extracts were lighter colored, and the dried residues were successfully ashed and counted without dilution. The $HClO_4$ extracts were counted without additional treatment.

In the calculation of amounts of ^{99}Tc extracted, corrections were made for (1) entrapped solution, (2) soil losses on filtration, (3) dilutions, if any and (4) quenching on counting.

Effect of soil sterilization on ^{99}Tc sorption: Earlier results suggested that sorption of ^{99}Tc by soils may be related to microbial activity. A soil sterilization experiment was conducted to further pursue this possibility. For this purpose, sterilization by steam without pressure, or tyndallization (Schmidt, 1975), was recommended over other possible procedures since it results in less change in the treated soil (Parkinson et al., 1971). The soil and ^{99}Tc were sterilized separately in order to decrease the chances of complexation of technetium by products released from the soil by the sterilization process.

The procedure involved placing 2 g (oven-dry basis) of Bergland, Arveson or Nicollet surface soil in tared 50 ml polypropylene centrifuge tubes with screw closures. The soil was moistened with 2 or 3 ml of distilled water 1 day before beginning the sterilization process in order to promote spore germination and to insure better steam penetration. The tubes were covered with aluminum foil and reweighed. The covered tubes and contents were steamed in an autoclave unit (with the steam outlet valve open) for 1 hour each day on days 0, 1, and 3. Between steamings the tubes were stored at room temperature in the laboratory. This split sterilization procedure allows for germination of spores between heat treatments. After the third steaming, the covered tubes were reweighed to determine the amount of water in soil (this was needed to make dilution corrections later). The aqueous ^{99}Tc solution, tube caps and all glassware used to contain and transfer the solution were autoclaved.

Transfer of the solution (25 ml, 0.0025 μCi ^{99}Tc/ml) to the tubes was done with automatic pipeting devices using aseptic techniques in a sterile transfer room. The tubes were capped, reweighed and the necks covered with tape. The sealed tubes were then placed in a 25°C water bath.

Biweekly sampling commenced after 4 weeks and included 3 replicates for each soil at each sampling date. Sampling entailed centrifugation for 10 minutes at 15,000 rpm, filtration of the supernatant through Whatman #42 filter paper and liquid scintillation counting of 1 ml aliquots of the filtrate.

Effect of aeration of soil-water suspensions on sorption of ^{99}Tc:

Effect of aeration by open-bottle shaking: In order to determine whether previously observed ^{99}Tc sorption was associated with development of anaerobic conditions in the soil-water system, a similar experiment was conducted in which well-aerated conditions were maintained.

Two g (oven dry basis) of Bergland, Arveson or Nicollet surface soils were placed in tared 60 ml linear polyethylene bottles and 25 ml of an aqueous solution containing 0.0024 μCi ^{99}Tc/ml was added to each bottle. The bottles were sealed with their normal polypropylene screw caps which had been modified by drilling a hole through the top. A 4 cm length of 4 mm I.D. glass tubing was inserted into the hole to provide a pathway for gas exchange between the atmosphere and the soil-water suspension. The bottles were shaken continuously on a reciprocating shaker (160 excursions/minute) at room temperature. Evaporative losses from the bottles amounted to about 0.03 ml/day and were replaced by biweekly additions of distilled water.

Biweekly sampling included 3 replicates for each soil at each sampling date. Sampling entailed centrifugation for 10 minutes at 9000 rpm, filtration of the supernatant through Whatman #42 paper and liquid scintillation counting of 1 ml aliquots of the filtrate.

Effect of aeration by bubbling: An initial experiment was conducted in which 50 g of Bergland soil (oven-dry basis) was placed in a 1 liter polyethylene bottle along with a sufficient quantity of 0.0024 μCi ^{99}Tc/ml solution to yield a 1:12.5 (w:w) soil:solution ratio as used in the study where the suspensions were shaken in an open container. Air was continuously forced through each of the 3 containers at a rate of about 1200-1500 ml/min by individual aquarium pumps and a length of glass tubing inserted through the mouth to the bottom of the bottle. The mouths of the bottles were covered with aluminum foil and additions of distilled water were made to the bottles every other day to make up for evaporative losses. Sampling, conducted on an every other day basis for the first 3 weeks and at weekly intervals thereafter, consisted of pipetting off 5 ml of suspension, centrifugation, filtration through Whatman #42 filter paper and liquid scintillation assay of 1 ml aliquots of the filtrate. Further filtration through a 0.22 μm millipore filter showed no additional ^{99}Tc removal indicating that the described procedure was effective in removing all sorbed ^{99}Tc. This initial experiment was conducted at room temperature (22 ± 3°C).

Effect of temperature on ^{99}Tc sorption by soils: The effect of temperature on ^{99}Tc sorption by Bergland, Arveson and Nicollet surface soils was determined using the aeration by bubbling technique described above with temperatures controlled at 15 ± 0.02 and 25 ± 0.02°C.

Sorption of ^{99}Tc by different samples of the same soil type: The extent that ^{99}Tc sorption properties varied within a given soil type was examined by using 4 samples of Bergland and Nicollet surface soils collected from different sites. The soil samples were characterized for pH, texture, organic carbon and free iron oxide (expressed as Fe_2O_3) and used in ^{99}Tc sorption experiments again using the aeration by bubbling technique described above. The soil samples were maintained in a moist room condition at room temperature between collection and use.

Effect of inoculation, incubation and dextrose addition on sorption of ^{99}Tc: The effect of inoculation, incubation and dextrose additions on the sorption of ^{99}Tc were studied using samples of Nicollet subsurface soil. Studies were conducted under either anaerobic (closed bottle) or aerobic (aeration by bubbling) conditions as previously described. The soil samples were treated in one of the following ways: 1) Nicollet subsurface only, 2) Nicollet subsurface plus 1% Nicollet surface, 3) Nicollet subsurface plus 1% Nicollet surface and 0.2, 0.5 or 1.0 percent dextrose. The amendments were added dry and mixed with the soil. The amended soils were either used immediately in sorption experiments or were incubated for 10 days prior to use at a moisture content of 60% of field capacity (taken to be 0.1-bar moisture content).

Effect of methiolate on ^{99}Tc sorption by soil: The effect of methiolate on ^{99}Tc sorption by Nicollet subsurface was determined by using a subsurface soil sample that had been inoculated with 1% Nicollet surface soil and to which 1% dextrose was added. The amendments were added dry and mixed well with the soil. The soil was watered to 60% of its 0.1-bar water-holding capacity and incubated for 10 days. On the tenth day 0.01% methiolate was added to one sample of the soil. In addition to this treatment, a second sample using the amended subsurface soil was treated with an additional 1.0% dose of dextrose.

Plant Uptake of ^{99}Tc:

Uptake from simple solution: Initial experiments involving the uptake of ^{99}Tc from solution by corn (Zea mays L. var. "Minn 8201"), soybeans (Glycine max L. var. "Corsoy"), radishes (Raphanus sativus L. var. "Early Scarlet Globe"), oats (Avena sativa L. var. "Rodney"), barley (Hordeum vulgare L. var. "Nordic"), and wheat (Triticum aestivum L. var. "Era") were conducted in a growth chamber maintained on a 23°C - 16 hour day and 17°C - 8 hour night cycle. The plants were grown in polyester growth pouches on 1/4 strength Hoagland solution no. 2 (Hoagland and Arnon, 1950) with an EDTA-iron source. There were 6 plants per pouch for radishes, 4 for the small grains and 2 for corn and soybeans. Two weeks after planting the nutrient solution was removed and 50 ml of either distilled water or 0.5 mM $CaCl_2$ containing 1.0 μCi of ^{99}Tc (as NH_4TcO_4) was added to each pouch. This corresponds to 1.2 ppm Tc in solution since the specific activity of ^{99}Tc is 17.2 mCi/g. The pouches were returned to the growth chamber for 48 hours. At harvesting, the roots were rinsed with deionized water and blotted dry and the plants divided into roots and shoots. The electrolyte-free system was chosen to afford maximum opportunity for uptake, while 0.5 mM $CaCl_2$ is a commonly used supporting electrolyte in excised root-mineral studies (Epstein, 1972).

Uptake from irrigated and incubated soils: Initial greenhouse experiments dealing with soil culture included uptake of ^{99}Tc by wheat seedlings from 11 soils with a wide range of chemical and physical characteristics (Tables 1 and 2). The soils were either irrigated with ^{99}Tc labeled water as plant growth occurred, or the ^{99}Tc was applied and the soils incubated for 2 months prior to seeding. A modified Neubauer method (Dowdy and Larson, 1975) using about 20 seedlings per 300 g of soil (i.e. soil:sand mixture) was employed. The soil in each pot was adjusted to the 0.1-bar water holding capacity by daily additions of water. Both unfertilized soils, and soils fertilized at a rate equivalent to 120 lbs N, 60 lbs P_2O_5 and 60 lbs K_2O per acre-six inches were studied. There were three replications per treatment per soil.

In the irrigation studies, a total of 6.0 µCi of ^{99}Tc was added to the soil surface of each pot in 2.0 µCi increments on days 4, 9 and 13 after planting. All aerial portions of the seedlings above the coleoptile were harvested on day 17.

In the incubation studies, a total of 6.0 µCi of ^{99}Tc was applied by a layering procedure to 300 g of soil. The pots were then covered with aluminum foil and moist (0.1-bar) incubated at about 25°C for two months prior to seeding. Due to anomalous growth patterns observed, which will be discussed later, the seedlings on the unfertilized soils were harvested 19 days after planting, and those on the fertilized soil were harvested when 20% or more of the seedlings were in the 3-leaf stage (15-26 days after planting).

Effect of ^{99}Tc on germinating seeds and young seedlings: The potential toxic effects of ^{99}Tc on germinating seeds and young seedlings of wheat, barley, oats, radishes, soybeans, and corn were studied using the growth pouch procedure described earlier in this report. This involved germinating and growing seedlings in polyester growth pouches containing 50 ml of 1/3 strength Hoagland solution No. 2 (Hoagland and Arnon, 1950) containing an EDTA-iron source. There were 10 plants in duplicate pouches for radishes and wheat, 7 each for oats and barley, 5 for soybeans and 4 for corn. Pouches containing the seeds were placed in the dark to germinate for the first 3 days and then transferred to a growth chamber maintained on a 23°C - 16 hour day and 17°C - 8 hour night cycle. Evaporative losses were made up by daily additions of deionized water.

The following specific studies were conducted using this procedure:

a) ^{99}Tc was added to the growth pouches at the rate of 0, 0.025, 0.25, 1.0, 2.5, 5.0, 6.7 and 10 μCi/50 ml of Hoagland solution prior to planting and germination of the 6 crop species listed above. Since the specific activity of ^{99}Tc is 17.2 μCi/mg Tc, these additions of ^{99}Tc correspond to 0, 0.03, 0.3, 1.2, 3.0, 5.8, 7.8 and 11.6 μg Tc/ml of solution. On the 10th day after planting, the plants were harvested by separating roots from shoots and removing what remained of the seeds. The roots were rinsed with running deionized water and blotted dry. Plants were dried, weighed, ground and representative samples digested and counted for ^{99}Tc as described previously.

b) Wheat seedlings were germinated and grown as described in "a" above except that ^{99}Tc was added to the growth pouches at the rates of 0, 0.0125, 0.025, 0.05, 0.25 and 1.0 μCi/50 ml of Hoagland solution to more precisely determine possible ^{99}Tc toxicity effects at very low concentrations.

c) Wheat seedlings were germinated and grown in growth pouches containing 50 ml of 1/2 strength Hoagland solution for either 10 or 18 days under conditions similar to those described in "a" above. Either 1.0 or 5.0 μCi ^{99}Tc was added to each growth pouch on day 0, 2, 4, 6 or 8 after planting to determine the effect of time of addition on ^{99}Tc toxicity to the seedlings. Evidence for germination was first observed on day 1 after planting.

Tissue yield and ^{99}Tc uptake and distribution in mature wheat plants: Five wheat seeds were germinated in each of 3 pots containing 1000 g of a 2:1 sand:soil mixture (by wt.) using Bergland and Nicollet surface soils. Plants were thinned to 3 per pot on day 7 after planting and the plants grown either to maturity or to a point that it was obvious they were not going to produce seed. The plants were grown in a greenhouse and the soil in each pot was adjusted to 0.1-bar water holding capacity by daily additions of 1/10 strength Hoagland solution. Either 10 or 20 μCi ^{99}Tc was added to pots containing the two soils in either three equal increments of 3.33 or 6.7 μCi on days 7, 17 and 33 or in one increment on day 7 or day 33.

Plants growing in pots containing 20 μCi of ^{99}Tc in 6.67 μCi increments on day 7, 17 and 33 or a single 20 μCi addition on day 7 were harvested on day 69 since there was no indication of seed production. All other plants were harvested on day 78 after planting. At harvesting, fresh and dry weights were taken, samples of the leaves and seeds were ground and representative samples were digested and counted for ^{99}Tc. In instances where there was no seed production, the older and younger leaves were separated to get some indication of ^{99}Tc distribution in the top portion of the wheat plants. Younger leaves generally included the last 4 or 5 leaves to develop before harvest.

Preparation of plant tissue for analysis: Each harvested plant segment in both the solution and soil uptake studies were cut into small pieces and placed in tared glass vials. Wet weights were obtained, and the tissue placed in a 60°C oven for 24 hours for determination of total dry weight. Tissue was ground with an intermediate Wiley mill (Arthur H. Thomas Co., Philadelphia, PA.) to pass the 20-mesh screen and placed in small glass vials. The ground tissue was then 60°C dried for about 16 hours. After drying the vials were capped with moisture tight snap caps. Samples of plant material were taken from these vials for ashing and radioassay.

Movement of ^{99}Tc in soils:

Soil Thin Layer Chromatography and Soil Column Layer Chromatography: Traditionally ion and molecular transport in soil systems has been characterized via soil column leaching studies. However, soil columns have a number of disadvantages. They are difficult to pack in a realistic and reproducable form. Chemical channeling may occur between the soil and the glass tubing, and realistic moisture regimes are usually not achieved. Analysis is also troublesome as the column must be destroyed and compaction is inevitable. The technique is very time consuming and labor intensive. Reproducable results usually occur only with sandy soils of low organic matter content (Chapman et al., 1970).

Soil thin layer chromatography (TLC) and soil column layer chromatography (CLC) have been successfully used to monitor the movement of pesticides and radionuclides in soils (Helling and Turner, 1968; Chapman et al., 1970; Rhodes et al., 1970; Helling, 1971; Reeves et al., 1977). Soil TLC and soil CLC are consistent laboratory techniques using soil as the absorbent phase and water as the solvent. These methods of transport analysis give easily reproducable chemical leaching distribution patterns. The basic parameter resulting from these techniques is the R_f, or the distance of species movement in relation to water front movement.

R_f values are a fractional measure of the maximum distance through which a substance will move through a given soil (Rhodes et al., 1970). Another parameter, K_d, has been suggested to characterize radionuclide movement in addition to the R_f number (Reeves et al., 1977). The K_d or distribution coefficient incorporates the bulk density and porosity of the soil thin layer column with the R_f value. The relationship is of the form

$$K_d = (R_d - 1)n/p$$

where R_d, the retardation factor, is the reciprocal of R_f, n is the porosity and p is the bulk density. This equation is analogous to the basic chromatographic equation

$$1/R_f = 1 + A_sK_d/A_m$$

in which A_s and A_m are cross-sectional areas of the liquid and solid phases, respectively (Breener et al., 1965; Rhodes et al., 1970).

The advantages of utilizing soil TLC and soil CLC is the rapid, relatively inexpensive, and reproducable nature of the technique (Helling and Turner, 1968). These methods will best reflect the movement of the chemical species through soil aggregates under unsaturated conditions (Helling and Turner, 1968; Reeves, 1977). These conditions approximate field conditions in a more realistic manner than does saturated flow through soil columns. The primary disadvantage inherent in these chromatographic techniques is the loss of soil structure and the difficulty in quantification of unsaturated flow.

Helling has proposed that pesticide mobility could be standardized and classified on the basis of R_f values (Helling and Turner, 1968). For this study, the classification could be modified to characterize the ability of the selected soils to transport ^{99}Tc, based upon relative mobility in order of increasing movement. This system uses 5 R_f classes (class 1, R_f=0.0-0.09; class 2, 0.01-0.34; class 3, 0.35-0.64; class 4, 0.65-0.89, and class 5, 0.90-1.00). Class 1 denotes the soil system with the least mobility and class 5 denotes the system with greatest mobility.

The technique of CLC used in this project was developed by workers at Oak Ridge National Laboratory (Reeves et al., 1977). This method has several advantages over soil TLC including isotope isolation, decreased lateral diffusion, ease of extraction and analysis, use of more than one soil per chromatographic plate, and a more consistent manual application of the soil as a thin layer.

Soil Column Layer Chromatography Analysis of ^{99}Tc in Soils: To prepare the soil CLC plate, the soils were first sieved in order to attain a more homogeneous layer (Helling, 1971). Immediately before spreading the soil was slurried to a moderate fluidity, and then uniformly applied into the channels of a glass Kontes Chromaflex CLC plate (Reeves et al., 1977) with a stainless steel spatula. This plate, 20 x 20 cm, is a modified thin layer chromatography plate with nine separate channels, each 20 cm long, 1 cm wide, and 2 mm deep. Usually two soils of similar texture were applied to one plate, with each soil replicated with three columns. The soil within the replicated columns was very similar. No adhesive amendments were used because the soils adhered to the columns. The soil was allowed to air dry over night before development.

At 4 cm above the bottom of each soil channel, 0.023 μCi of ^{99}Tc was spotted with a disposable glass micropipet. The sample size of the spot is independent of the measured R_f value; however, the amount of trailing and lateral movement is related to the sample size (Helling, 1971). The spot of ^{99}Tc was allowed to air-dry before elution with distilled water. To prevent sloughing of the soils out of the channels into the eluting solution, chromatographic paper wicks were placed over the end of each channel (Reeves et al., 1977). The wicks were approximately 7 mm x 4 cm and placed over the first centimeter of soil. The wicks were held in place by a conventional TLC plate clamped over the CLC plate with metal binding clips.

The plates were then positioned in an aluminum development stand with the wicks resting on the bottom of an enamel or nylon water pan. The plates were held at an angle of 68^o to the horizontal water surface (Reeves et al., 1977). Distilled water was poured into the pan and was wicked up to the soil thin layer columns simultaneously. With water ascending chromatography, plate development is continued until the water front reaches the 10 cm level above the spot location. However, with two soils on a given plate this was not always possible because the rate of water movement in one soil often exceeded that in the other. The criteria for termination of development was to stop elution when the slower water front reached 10 cm. In some cases development was stopped when the faster water front approached the top of the plate. The difference in height of water rise in the column is not crucial (Helling, 1971). The plate development time was recorded.

Two methods for analysis of isotope distribution were used, autoradiography and column dissection with extraction. The autoradiographic technique was used as a qualitative measure of ^{99}Tc distribution and R_f. Dissection and extraction of successive 1 cm zones of the soil channels allowed the determination of quantitative distribution parameters. These parameters include R_f, the ratio of total isotope movement to water front movement; R_p, the ratio of peak isotope movement to water front movement; and R_b, the ratio of movement of the bottom of the isotope distribution to water front movement (Rhodes, 1970). All distances were measured relative to the top of the original ^{99}Tc spot at 4 cm.

The qualitative autoradiographic analysis provided substantiation for distribution parameters obtained by the dissection and extraction method. After the developed CLC plate had air-dried it was wrapped in cellophane to prevent any contamination of the film package. Kodak No Screen NS-2T X-Ray film was then secured between the covered soil CLC plate and a conventional glass TLC plate. The film was exposed for 48-72 hours in a darkened laboratory drawer and developed with standard Kodak developing solutions.

The dissection and extraction technique was more rigorous. Immediately after eluting the soil CLC plate each column was dissected into 1 cm fractions. Dissection and removal of soil was done with a pointed stainless steel spatula. The individual soil segments were placed in separate 17 x 100 mm polypropylene Falcon tubes (#2059). This procedure was followed for the ten major mineral soils characterized for this project. For the soils characterized by Pluth, the soil segments from the same zone on the replicate columns were all placed in the same Falcon tube.

The gravimetric water content was determined for each soil sample. This was done by weighing the wet soil segments immediately after the plate dissection, drying at 105° C for twelve hours, and weighing again. The gravimetric water content was determined as

$$\theta_w = \frac{\text{Wet weight of soil - Dry weight of soil}}{\text{Dry weight of the soil}}$$

Using the total soil weight and the previously measured soil volume the dry bulk density of the soil in the columns was determined as

$$D_b = \frac{\text{Dry weight of the soil}}{\text{Volume of the soil}}$$

Corrections were made for the small residual soil left on the plate after dissection in order to compute more realistic bulk densities.

Porosity is a significant parameter for the determination of the K_d value. Porosity was determined by the following equation (Vomocil, 1965)

$$\text{Porosity} = 1 - (\text{Bulk Density}/\text{Particle Density}).$$

Particle density was determined for all the soils by the method of Blake (1965).

After the soil fractions were weighed, 10 ml of 0.01M CaCl$_2$ was pipetted into each tube to extract the ^{99}Tc. The soil and solution were mixed for one minute on a Vortex-Genie. The samples were then centrifuged at 12,000 RPM for ten minutes. A 1 ml aliquot of the supernatant solution was then transferred into a previously described scintillation vial. Ten milliliters of the basic scintillant was added and the samples were counted for 10 to 20 minutes.

The remainder of the CaCl$_2$ supernatant solution was discarded and 10 ml of 0.01M NaOH was added to each tube. The amount of solution remaining in the tube from the first extraction was accounted for in the analysis. After the addition of NaOH, samples were shaken overnight and activity determined in the same manner as in the CaCl$_2$ extraction. In a preliminary experiment, we determined that a second CaCl$_2$ extraction was as effective in removing the residual ^{99}Tc as was the extraction with NaOH.

Quench corrections and counting efficiencies were made for each individual soil and extraction using a spiked soil sample. This sample was the same average weight as the soil fractions and underwent similar extraction treatments. A known spike of ^{99}Tc was added to the scintillation vial with the aliquot of extractant from the blank. The background was determined using a similar soil sample subjected to the extraction procedures but with no spike added to the scintillation vials.

The soil fractions were small enough so that dissolved organic matter from the NaOH extraction did not cause excessive quenching.

The amount of ^{99}Tc present at each column position was determined as the percent of the original amount of ^{99}Tc added to the thin-layer column. This was done for both the $CaCl_2$ and NaOH extraction. The recovery rate for the $CaCl_2$ extraction was very high, and only these results will be discussed. The NaOH extracted only the residual $CaCl_2$ in the tube.

Using one-way analysis of variance, a mean deviation or position error was determined for the ten soils characterized for the sorption study. This was possible because the three replicate columns were analyzed for these soils. The mean position deviation is the square root of the mean square error from analysis of variance for a given soil. This error was used as the criterion for the realistic presence of the pertechnate anion. ^{99}Tc is considered present only in those soil column fractions in which the percent of ^{99}Tc exceeds the criterion of Mean Square Error$^{\frac{1}{2}}$/Number of Replicates$^{\frac{1}{2}}$. This criterion is analogous to a standard error.

In order to project the position error for the soils extracted in bulk, multiple regression analysis was used to relate calculated position errors to known soil physical, chemical, and chromatographic parameters. The mean position errors for the soils characterized by Pluth were then predicted. It should be noted that for those soils with R_f values significantly different from unity, the percent of ^{99}Tc in the highest soil segment was considerably less than the projected criterion, indicating ^{99}Tc had not reached that segment.

Soil Column Layer Chromatography with ^{36}Cl: To compare the mobility of the pertechnate ion to the movement of another anion, six soils were selected with variable ^{99}Tc R_f values and monitored for the movement of ^{36}Cl. The chloride ion would model as anion movement through the soil. The soils selected were six surface soils including Nicollet, Hibbing, Ulen, Canisteo, Brainerd, and Kranzburg.

The ^{36}Cl was obtained from New England Nuclear as a 0.2-3.0M HCl solution with > 99% purity.

Basically the same procedure was used for preparation, elution, and extraction of the soil CLC with ^{36}Cl as for ^{99}Tc. The only difference was that the qualitative autoradiographic analysis was not performed and 0.020 μCi of ^{36}Cl was spotted at the 4 cm position. Again quench corrections and counting efficiencies were obtained with a spiked blank soil sample. The replicated column segments were combined to obtain the mean percent of ^{36}Cl of the total originally added to the columns. The second extraction with NaOH was not carried out.

The same scintillant was used for counting the ^{36}Cl. The ^{36}Cl was determined with the same Packard liquid scintillation spectrometer as the ^{99}Tc. The discrimination setting was from 50-1000 and the amplification was at 1.2%. ^{36}Cl is a beta particle emitter with an E_{max} of 0.712.

Soil Column Leaching of ^{99}Tc: The six soils employed in the ^{36}Cl soil CLC analysis were also used in column leaching studies with ^{99}Tc. The air-dry soil was packed into 1 cm diameter glass tubing to the depth of 5 cm. The soil was held in place with 0.5 cm of packed glass wool at the bottom of the cylinder. The dry bulk density of the soil was computed based on the weight of the soil and the volume of the glass tube. The soil weight was corrected for water content.

After packing and the determination of bulk density, the soil column was connected to a suction filter flask through a rubber stopper in the bottom of the soil column. The glass suction filter flask was connected to a constant source of suction controlled by a Gast Vacuum Gauge. The connecting glass tubing between the soil column and filter flask was directed into a scintillation vial to collect the solution leaching through the soil column.

Before beginning the column leaching of ^{99}Tc the soil column was allowed to wet for at least three hours. After thorough wetting of the soil at least 5 separate 1 ml aliquots of 0.005<u>M</u> $CaCl_2$ were passed through the column under a constant suction of 1/10 bar for sandy soils and 1/3 bar for silty and clayey soils. The fourth and fifth aliquot were saved as the background blank and the spiked sample for quench correction and counting efficiency determination. The one milliliter aliquots of the leaching solution pass through the column. The suction and $CaCl_2$ solution concentration were chosen to approximate field leaching conditions.

After the two blank samples were collected from the soil column, 0.0213 μCi of ^{99}Tc was spotted at the top of the column with a disposable glass micropipet. There was no suction on the column at this time. Then under constant suction, fifteen 1 ml aliquots of 0.005<u>M</u> $CaCl_2$ were leached through the column. Each fraction was allowed to move freely through the column and into the scintillation vial in the bottom of the filter flask. This process continued for each aliquot until drainage ceased. The time required for the one milliliter aliquots to pass through the soil ranged from 10 minutes to one hour. The scintillation vials were placed and removed from the filter flask with slender aluminum tongs.

Fifteen successive aliquots of the $CaCl_2$ leaching solution passed through all the soil columns except those of the Hibbing surface soil. Due to the time necessary for each aliquot to pass through the column (1 hour), only eight fractions were passed through the three Hibbing soil columns. However, over 95% of the original ^{99}Tc added to the columns was recovered. The samples of leachate from the soil columns were counted as previously described for the soil CLC plates.

RESULTS AND DISCUSSION

Soil characterization:

The soil samples, all of which were taken in the state of Minnesota (Fig. 1), had a wide range of physical and chemical properties such as texture, pH, organic matter, free iron oxide content and cation exchange capacity (CEC) as shown in Tables 1 and 2. While the mineralogic composition of these particular samples was not determined, a study by Pluth et al. (1970), of the characteristics of selected horizons from 16 soil series sampled throughout the state of Minnesota reveals similar mineralogy in the $<5\mu$ fraction despite widely ranging physical and chemical properties. The fine silt (5-2μ) fractions were the most heterogeneous with mica, kaolinite, quartz and feldspars. The fine clay ($< .2\mu$) fractions proved to be the least heterogeneous in mineralogic composition, being dominated by montmorillonite with small amounts of mica and kaolinite.

Sorption of ^{99}Tc by soils:

Sorption of ^{99}Tc by whole soils: Eight of the 11 soils studied sorbed over 98% of the added ^{99}Tc from aqueous solution at 25°C (Fig. 2). (Bars about the plotted points in this and other figures represent ± one standard error about the mean.) However, periods of 3 to 5 weeks were required for this sorption to take place. In contrast to the other soils, Nicollet subsurface and Zimmerman surface soils showed very little sorption during the same period of time, and the Hegne soil showed about 70% sorption. Both the Nicollet subsurface and Zimmerman surface soils have low organic matter contents, indicating the sorption of ^{99}Tc may be directly or indirectly associated with that fraction of the soil. Solution pH was measured at the time of sampling. However, no trends in sorption (or lack of sorption) versus pH were evident.

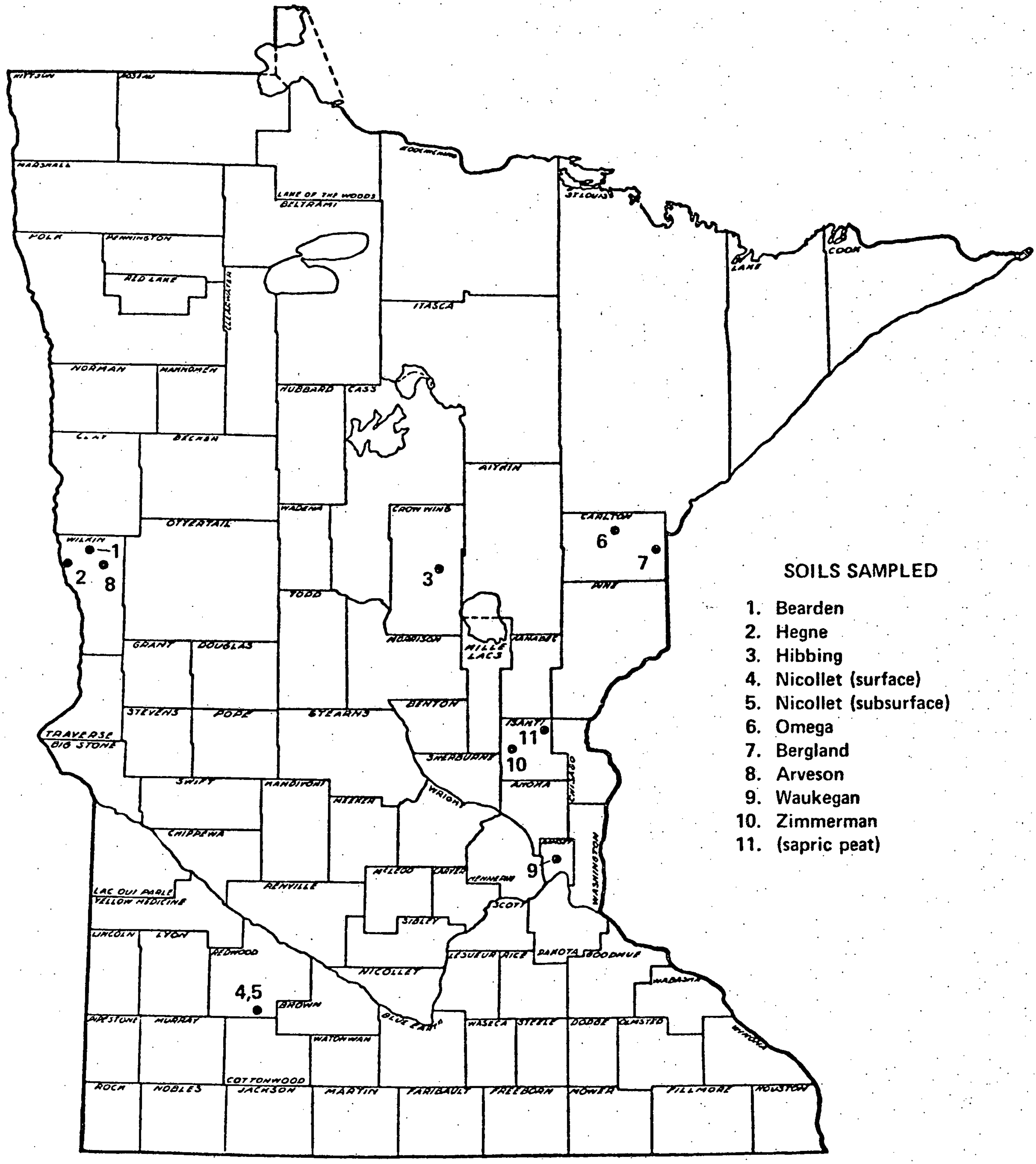


Fig. 1. Location of sampling sites

Table 1. Physical properties of soils used in ^{99}Tc sorption and plant uptake studies.

Site no.	Soil Series	Subgroup Classification	Location (Minn. Co.)	Depth Sampled (inches)	-------Texture----- %sand	%silt	%clay	Surface Area(2) m^2/g,	Water Retention g_{H_2O}/g_{OD} Soil 1/3 bar	15 bar
1.	Bearden	Aeric Calciaquoll	Wilkin	0-10	9.1	63.7	27.2	91.8	0.26	0.15
2.	Hegne	Typic Calciaquoll	Wilkin	0-10	1.9	37.6	60.5	287.3	0.37	0.23
3.	Hibbing	Typic Eutroboralf	Crow Wing	0-8	3.3	79.5	17.2	46.5	0.32	0.13
4.	Nicollet (surface)	Aquic Hapludoll	Redwood	0-8	27.4	42.9	29.7	144.4	0.27	0.14
5.	Nicollet (subsurface)	Aquic Hapludoll	Redwood	60-66	23.9	48.6	27.5	153.1	0.25	0.13
6.	Omega	Spodic Udipsamment	Carlton	0-4	61.5	30.7	7.9	32.5	0.12	0.05
7.	Bergland	Aeric Haplaquept	Carlton	0-7	14.0	25.1	60.9	222.0	0.40	0.30
8.	Arveson	Typic Calciaquoll	Wilkin	0-9	47.1	24.6	28.3	98.6	0.22	0.13
9.	Waukegan	Typic Hapludoll	Ramsey	0-6	10.0	69.2	20.7	89.1	0.26	0.14
10.	Zimmerman	Alfic Udipsamment	Isanti	0-6	69.4	24.9	5.7	16.5	0.05	0.02
11.	Undesignated (peat)	Borosaprist (1)	Isanti	0-4	----	----	----	----	2.42	0.95

(1) Great Group

(2) Mineral Fraction only

Table 2. Chemical properties of soils used in ^{99}Tc sorption and plant uptake studies.

Site no.	Soil Series	pH H_2O	pH KCl	% Organic Carbon	%$CaCO_3$ equivalent	Free iron oxide (%Fe_2O_3)	C.E.C. (meq/100g.)	Extractable P (lbs/acre) -6"	Exchangeable K (lbs/acre) -6"
1.	Bearden	7.68	7.38	5.39	16.29	0.09	16.9	17	530
2.	Hegne	8.00	7.20	2.20	12.79	0.29	36.1	8	540
3.	Hibbing	5.48	4.18	2.29	---	1.40	11.3	7	140
4.	Nicollet (surface)	5.91	5.07	2.39	---	0.86	19.3	8	220
5.	Nicollet (subsurface)	8.40	7.53	0.12	15.21	1.35	15.7	9	140
6.	Omega	7.87	7.38	1.26	1.21	1.20	6.0	183	430
7.	Bergland	6.35	5.47	5.67	---	2.39	32.3	20	460
8.	Arveson	7.70	7.35	2.80	15.58	0.21	14.9	8	230
9.	Waukegan	6.25	5.38	2.36	---	1.03	15.1	182	470
10.	Zimmerman	5.74	4.72	0.80	---	0.47	2.7	79	70
11.	Undesignated (peat)	7.83	7.49	45.95	7.58	0.40	50.9	24	150

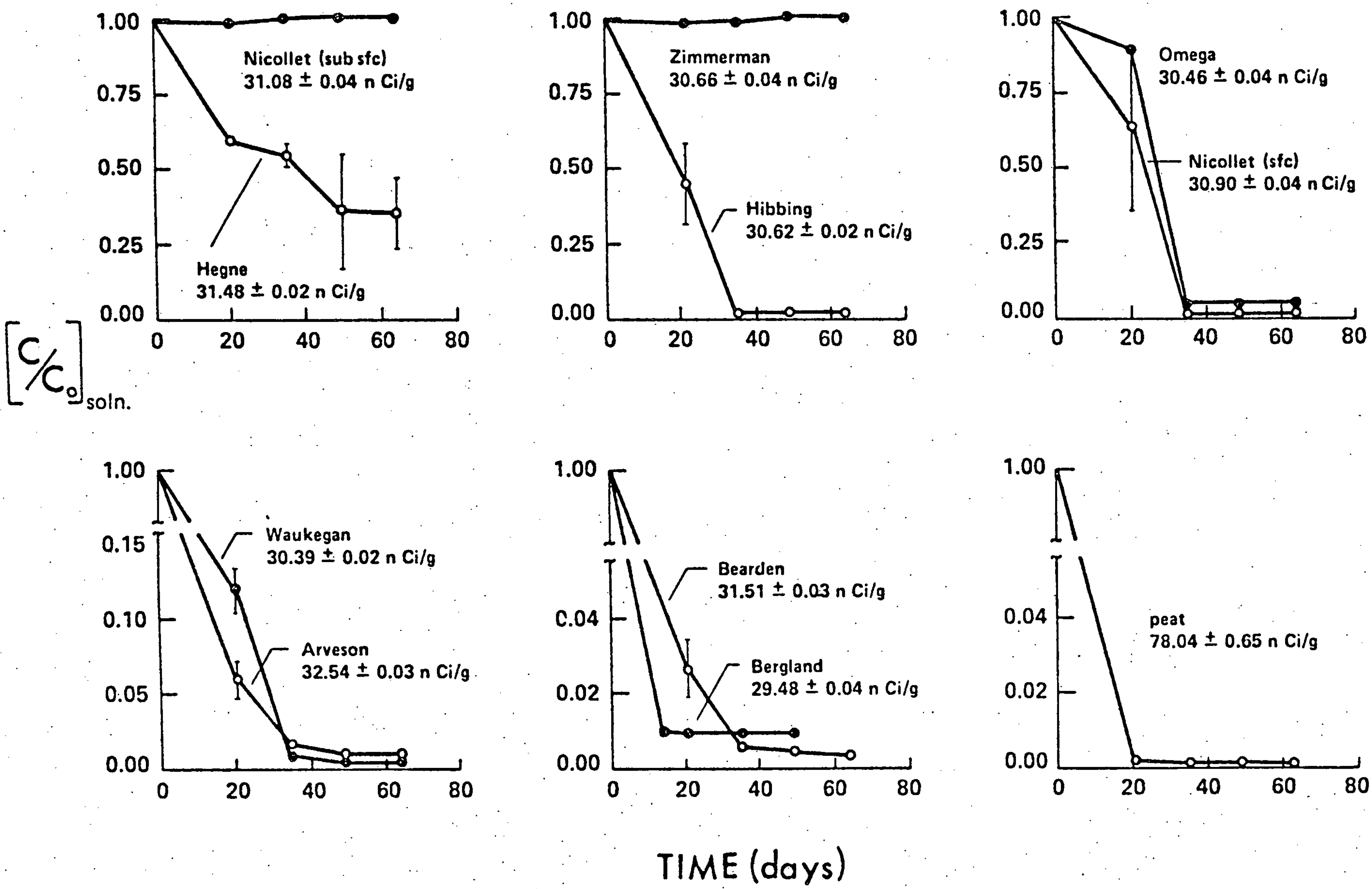


Fig. 2. Sorption of ^{99}Tc by whole soils at 25°C. Values represent the means of duplicate samples with standard errors of the means indicated by brackets.

Effect of selective dissolution treatments on sorption of ^{99}Tc: Hydrogen peroxide digestion of the relatively high organic matter Bergland soil essentially stopped sorption of ^{99}Tc (Fig. 3), further indicating that the organic fraction of the soil is in some way involved in the sorption process. The dithionite treatment also reduced sorption (Fig. 3) in this soil suggesting that free iron oxides may also be involved. However, the possibility of either of these treatments having other effects such as reducing microbial activity cannot be ruled out.

Effect of increasing ^{99}Tc levels on sorption by soils: Based on a specific activity of 17.2 mCi ^{99}Tc per g of Tc and assuming that Tc remains in the form of the pertechnetate ion, the addition of 30 nCi of ^{99}Tc per g of soil is equivalent to adding 0.018 μeq of TcO_4. While it might be expected that this very small quantity is well below the anion sorption capacity of soils, sorption of increasing quantities of ^{99}Tc was determined to establish that this is the case. Increasing the amount of ^{99}Tc added from 30 to 3000 nCi/g did have some effect on the kinetics of sorption by Bergland soil (Fig. 4), but more than 98% of the added ^{99}Tc was eventually sorbed in all cases. These results indicate that the 30 nCi/g added in most of the experiments is probably well below the sorption capacity of the soils.

Effect of KCl and KH_2PO_4 on ^{99}Tc sorption by soils: Since the ^{99}Tc was added as the TcO_4^- ion in relatively small quantities, one of the most likely sorption mechanisms is anion exchange. In addition, the possibility exists that the TcO_4^- ion may be specifically adsorbed by the process of ligand exchange on oxide surfaces as in the case of phosphorus. If anion exchange is involved, the addition in excess of Cl^- should reduce the amount of sorption. As can be seen in Fig. 5, the addition of KCl

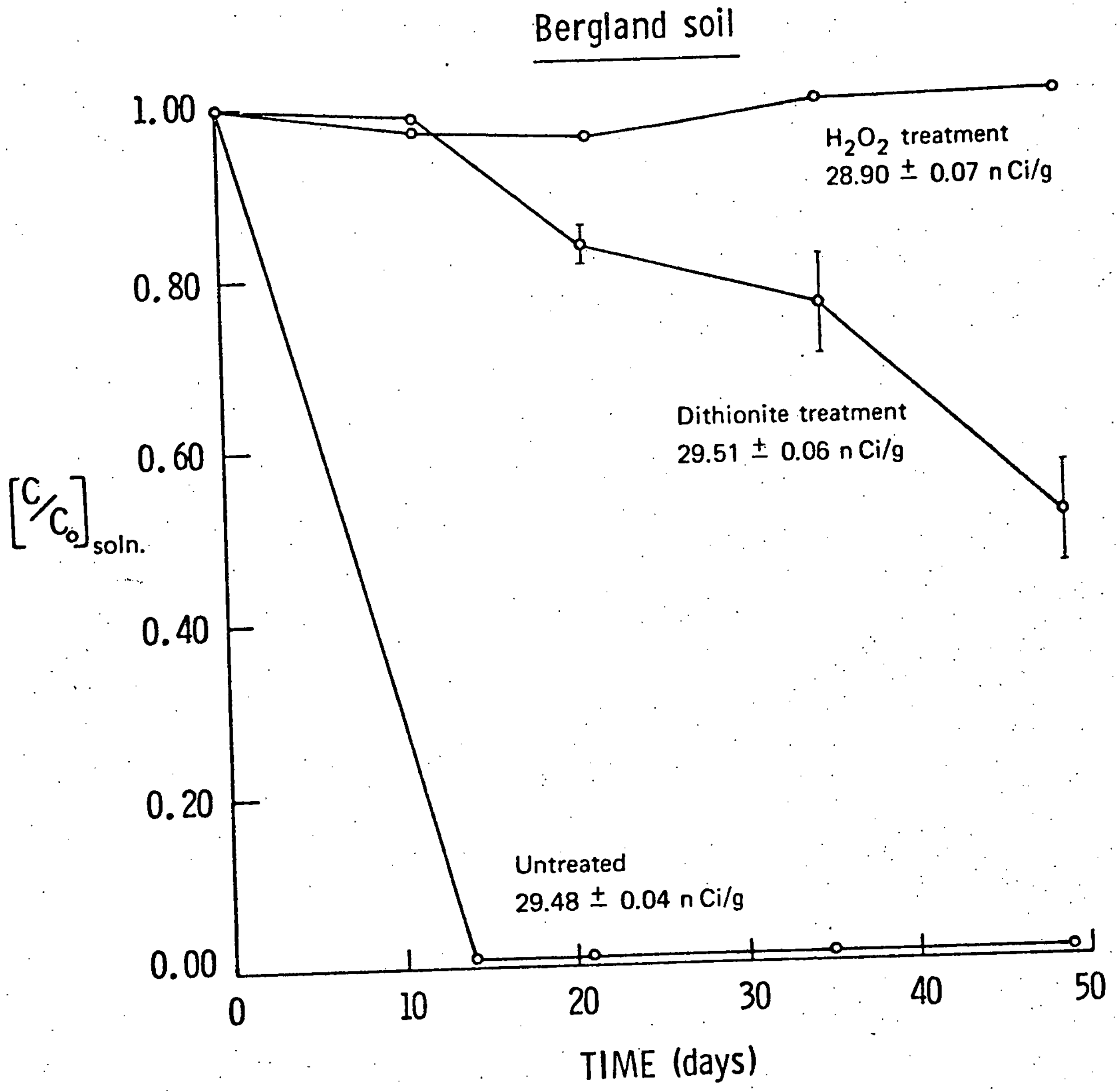


Fig. 3. Effect of pretreatment of soil with hydrogen peroxide and sodium dithionite on sorption of ^{99}Tc by Bergland soil from water at 25°C. Values represent the means of duplicate samples with standard errors of the means indicated by brackets.

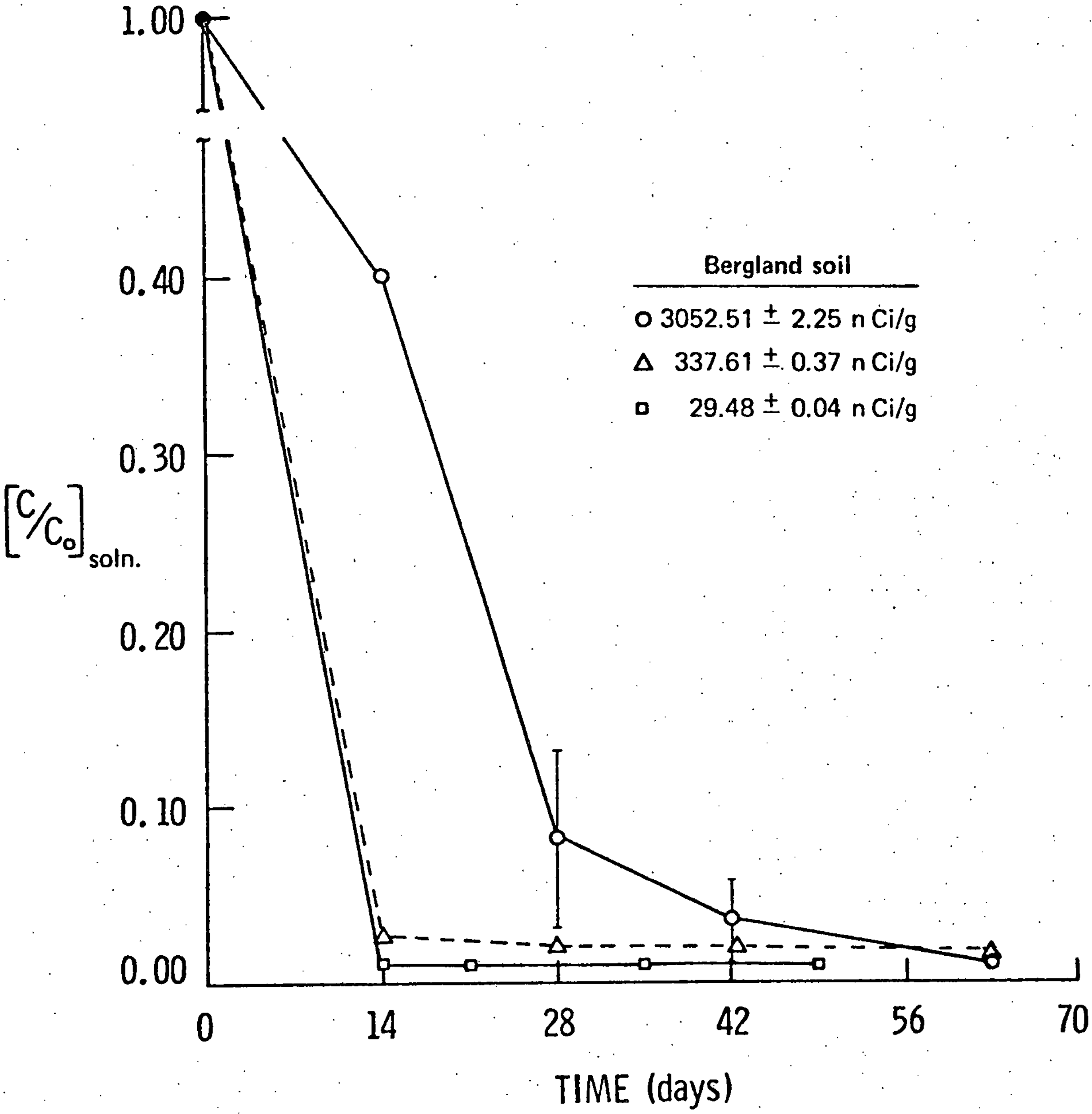


Fig. 4. Effect of ^{99}Tc concentration on sorption by Bergland soil at 25°C. Values are the means of duplicate samples with standard errors of the means indicated by brackets.

did not have any significant effect indicating that anion exchange is not the sorption mechanism involved in these particular studies. Similarly it might be expected that an excess of $H_2PO_4^-$ might interfere with ^{99}Tc sorption if specific adsorption mechanisms are involved. Since this was not the case (Fig. 5), some mechanism other than specific adsorption is apparently involved.

Extraction of sorbed ^{99}Tc from soils: Results of the extraction experiments (Table 3) show that most, if not all, of the ^{99}Tc which was removed from solution during the sorption experiments was sorbed by the soil rather than being lost by volatilization. Sodium hydroxide proved to be a more efficient ^{99}Tc extractant than perchloric acid in all cases except the Omega soil. These high removals with alkali further suggest a role for organic matter in the sorption of technetium by soils.

Effect of soil sterilization on ^{99}Tc sorption: The relatively slow kinetics of sorption suggests that the loss of ^{99}Tc from solution might be related to microbial activity. This suggestion is further substantiated by the effect of soil sterilization which eliminated ^{99}Tc sorption by the Nicollet, Bergland and Arveson surface soils (Fig. 6). Since alteration of soils by the tyndallization process is minimal, it appears that the observed sorption of ^{99}Tc by soils is in some way associated with microbial activity. This association may involve incorporation of ^{99}Tc into microbial tissue, interaction with microbial metabolites, or perhaps effects associated with the depletion of dissolved oxygen by microbial metabolism.

The exact role of microbial uptake is difficult to evaluate in light of the absence of data on soil microorganisms. Gearing et al. (1973, 1975) have demonstrated some binding of ^{99}Tc by pertechnetate-exposed algae. Also, microbial metabolites may reduce Tc^{7+}-pertechnetate to a lower valence state species capable of binding to soil organic matter.

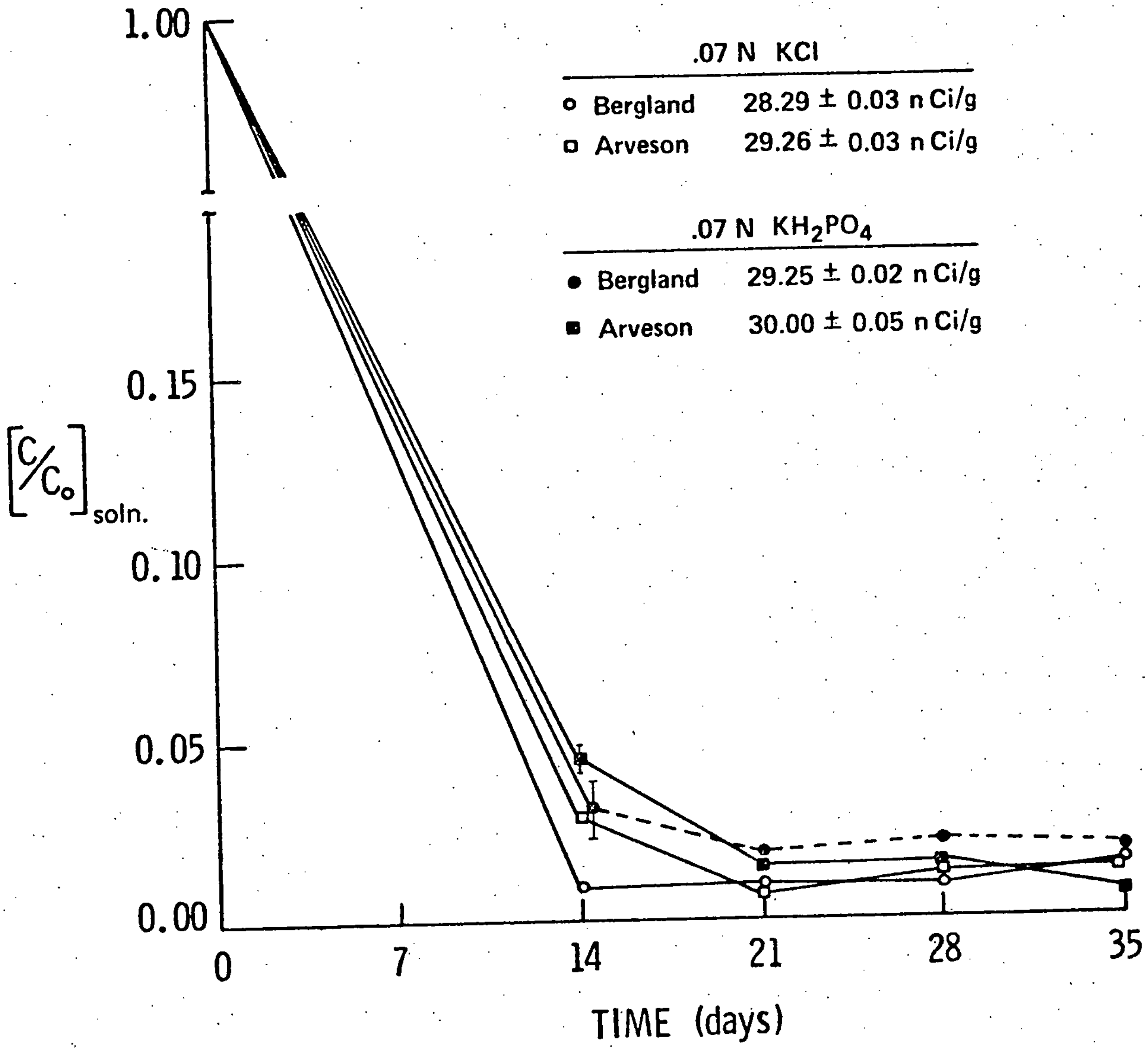


Fig. 5. Effect of .07N KCl and .07N KH_2PO_4 on sorption of ^{99}Tc by Bergland and Arveson soils at 25°C. Values are the means of duplicate samples with standard errors of the means indicated by brackets.

Table 3. Extraction of sorbed ^{99}Tc from soils by 1.0 N $HClO_4$ and 1.0 N NaOH. Tabulated values are the means of two replicates with the standard errors of the means indicated in parentheses.

Soil and Extractant		% of added ^{99}Tc sorbed prior to extraction	% of sorbed ^{99}Tc extracted				
			Extraction Number				Total (All extractions)
			1	2	3	4	
Hegne	$HClO_4$	99 (0.2)	24 (9.7)	9 (2.6)	7 (0.6)	5 (0.03)	45 (13.0)
	NaOH		86 (1.7)	4 (0.06)	2 (0.05)	1 (0.01)	93 (1.7)
Nicollet (surface)	HClO	93 (1.0)	48 (0.3)	15 (0.3)	8 (0.3)	5 (0.1)	76 (1.0)
	NaOH		99 (2.8)	2 (0.2)	1 (0.2)	0.7(0.04)	103 (2.4)
Omega	$HClO_4$	20 (0.1)	100 (0.4)	4 (0.2)	1.4(0.09)	0.8(0.06)	106 (0.7)
	NaOH		78 (0.04)	7 (0.6)	3 (0.1)	2 (0.08)	91 (0.6)
Bergland	$HClO_4$	98 (0.1)	12 (0.1)	7 (0.3)	5 (0.07)	4 (0.1)	27 (0.6)
	NaOH		77 (3.3)	9 (2.0)	2 (0.2)	0.8(0.1)	89 (1.0)
Arveson	$HClO_4$	98 (0.1)	7 (0.01)	3 (0.04)	2 (0.04)	2 (0.01)	14 (0.02)
	NaOH		83 (1.0)	5 (0.07)	2 (0.1)	1 (0.07)	92 (1.0)
Peat	$HClO_4$	99 (0.1)	2 (0.1)	0.6(0.05)	0.8(0.08)	0.9(0.1)	4 (0.3)
	NaOH		50 (0.9)	*0.05(0.02)	6 (0.2)	6 (0.2)	63 (0.5)

* Sample did not disperse initially after 15,000 rpm centrifugation. Subsequent peat extractions centrifuged at 5000 rpm.

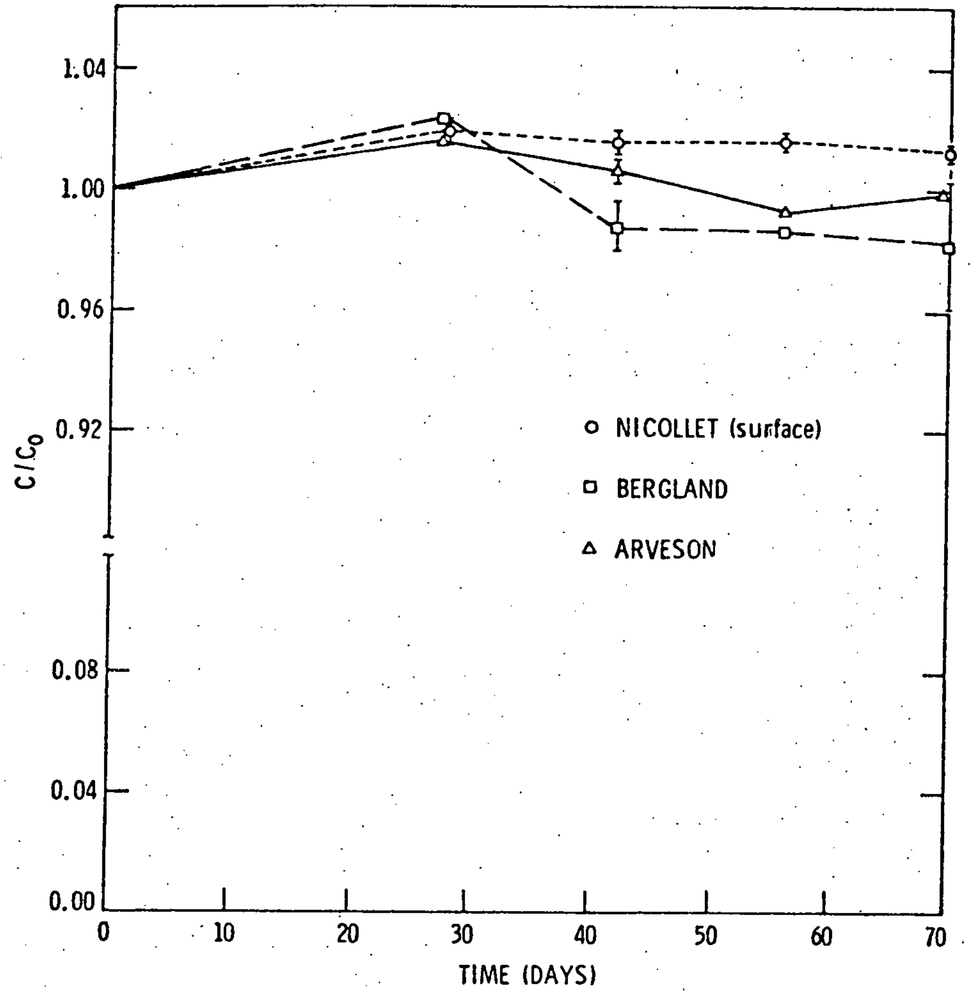


Fig. 6. Effect of steam sterilization pretreatment of soils on sorption of ^{99}Tc by soils from water at 25°C. Values represent the means of triplicate samples with standard errors of the means indicated by the brackets.

The reduction of Tc^{7+} to Tc^{4+} by ascorbic acid, for example, is a commonly used procedure in the preparation of radio-pharmaceuticals. Such reduced technetium species can bind irreversibly to proteins, probably by covalent bonding (Dewanjee, 1974).

Effect of aeration on ^{99}Tc sorption by soils: The use of previously air-dried soil in dense-walled, tightly-sealed bottles are conditions conducive to the development of high microbial respiration rates and subsequent depletion of dissolved oxygen (Avnimelech and Raveh, 1974). Precipitation of technetium as Tc_2S_7 could result from H_2S production by anaerobic sulfate-reducing bacteria. Also, a drop in Eh could result in mobilization of metals capable of reducing pertechnetate to a species capable of organic matter binding as discussed above.

The bubbling and shaking experiments were established to see if aeration of the system would have any effect on sorption. Similar aeration methods have been used by Molina et al. (1971) in studying aeration-induced changes in liquid-digested sewage sludge. Results of the shaking experiment are shown in Fig. 7. In contrast to the sealed-bottle study (Fig. 1), the Nicollet surface soil exhibited no sorption of ^{99}Tc over the 12 week period. The Bergland exhibited an initial high removal of ^{99}Tc from solution, such as observed in the earlier sealed-bottle studies, but then showed a progressive reduction in sorption from the second to the twelfth week. The Arveson soil showed an erratic sorption pattern with from 50 to 80% of the added ^{99}Tc remaining in solution over the 12 week period.

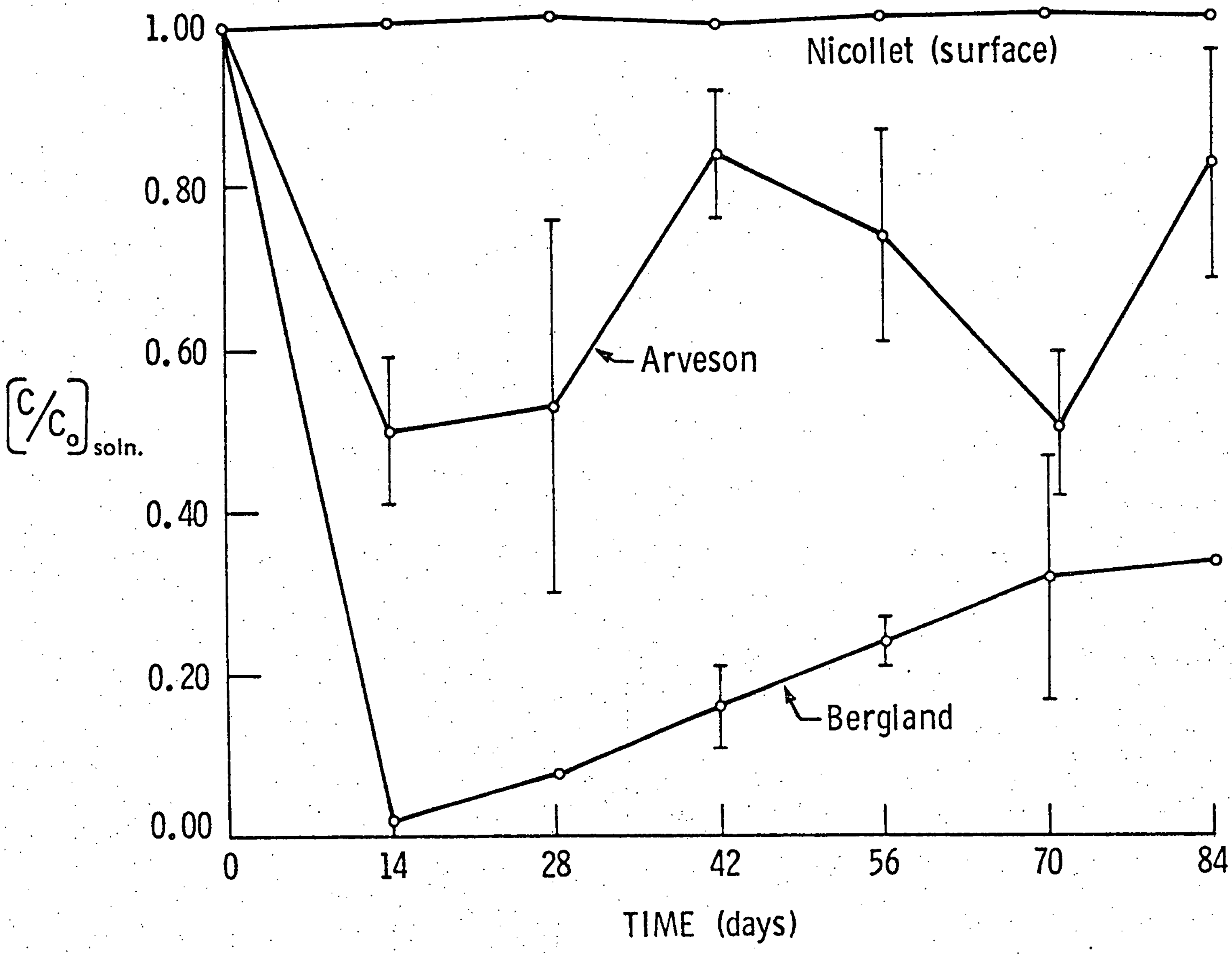


Fig. 7. Effect of aeration (by open-bottle shaking) on ^{99}Tc sorption by soils from water at ambient temperature. Values represent the means of triplicate samples with standard errors of the means indicated by brackets.

While one intuitively felt that these suspensions were aerobic, the oxygen status of the suspensions employed in the third sampling of the shaker aeration study was checked with a YSI model 54 oxygen meter (Yellow Springs Instrument Co.; Yellow Springs, Ohio). These suspensions all showed dissolved oxygen levels corresponding to between 80 to 90% of that measured for unstirred air-saturated water.

Results of the 25°C bubbling experiment with the Bergland soil are shown in Fig. 8. While removal appears to be slower than observed in the sealed bottle experiments, the solution concentration of ^{99}Tc progressively decreased to about 10% of the initial concentration after 2 months.

The differences in sorption behavior exhibited for the individual soils between the closed and open bottle systems, and between the soils in these open systems are difficult to explain. Nevertheless these aeration trials suggest that anaerobic conditions are not required for ^{99}Tc sorption by soils. The effects observed may be related to the stability of a reduced technetium species exposed to oxygen (e.g. Eckelman <u>et al</u>., 1971), or perhaps to variations in microbial flora present at various oxygen tensions.

Effect of temperature on ^{99}Tc sorption by soils: There was a decrease in ^{99}Tc sorption by the Arveson and Bergland soils at 15°C compared to that at 25°C (Fig. 9), further indicating that the sorption of ^{99}Tc is probably related to microbial activity rather than a purely chemical process; i.e. the amount of sorption by chemical processes should increase as temperature is lowered. The Arveson soil showed sorption levels intermediate between the Bergland and Nicollet soils at 25°C (Fig. 9) as was found in the open-bottle shaking experiment. It also showed less sorption at 15°C than at 25°C suggesting again that a microbially related process is involved. The Nicollet surface soil showed relatively little sorption compared to the Bergland and Arveson

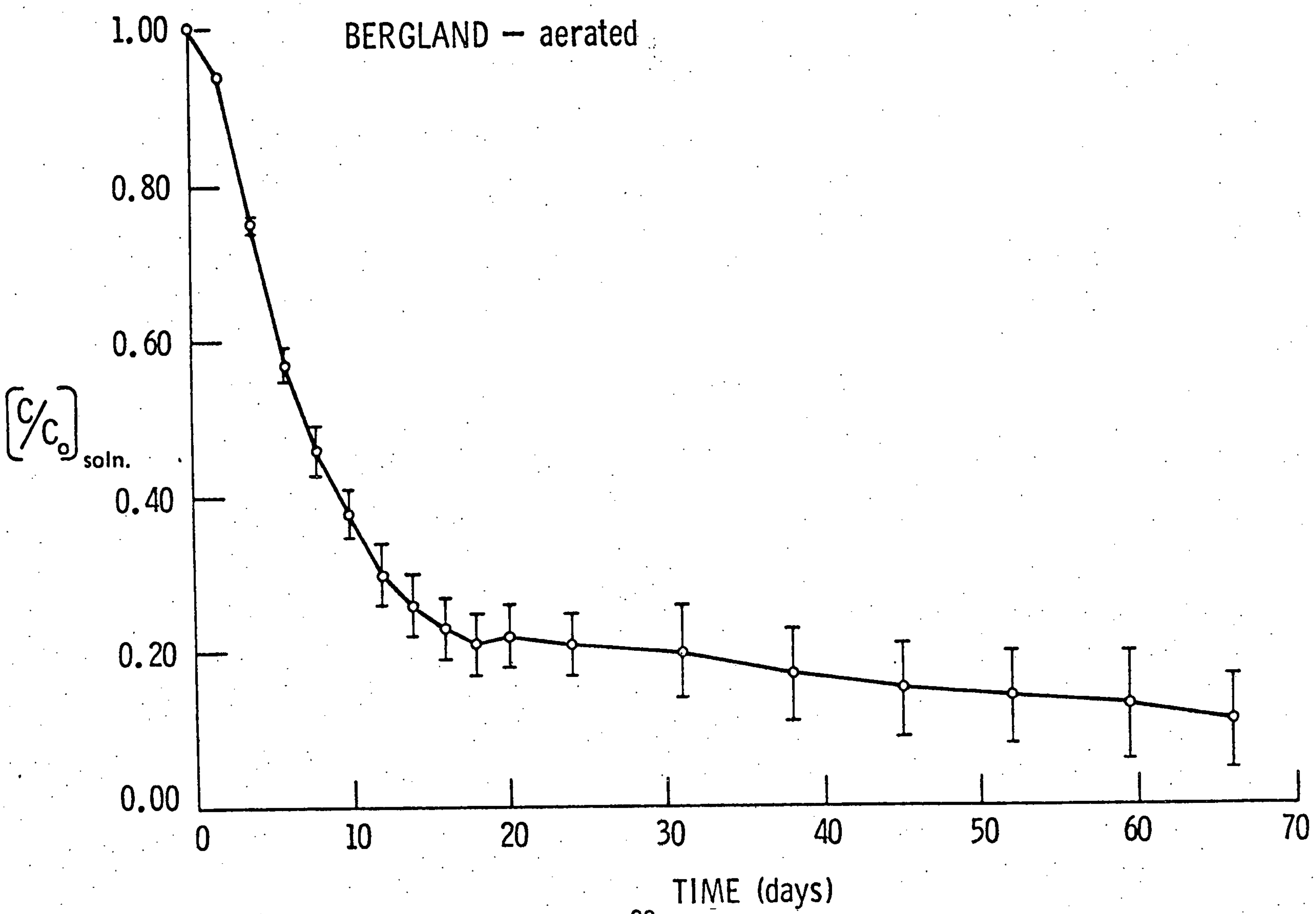


Fig. 8. Effect of aeration (by bubbling) on ^{99}Tc sorption by soils from water at ambient temperature. Values represent the means of triplicate samples with standard errors of the means indicated by brackets.

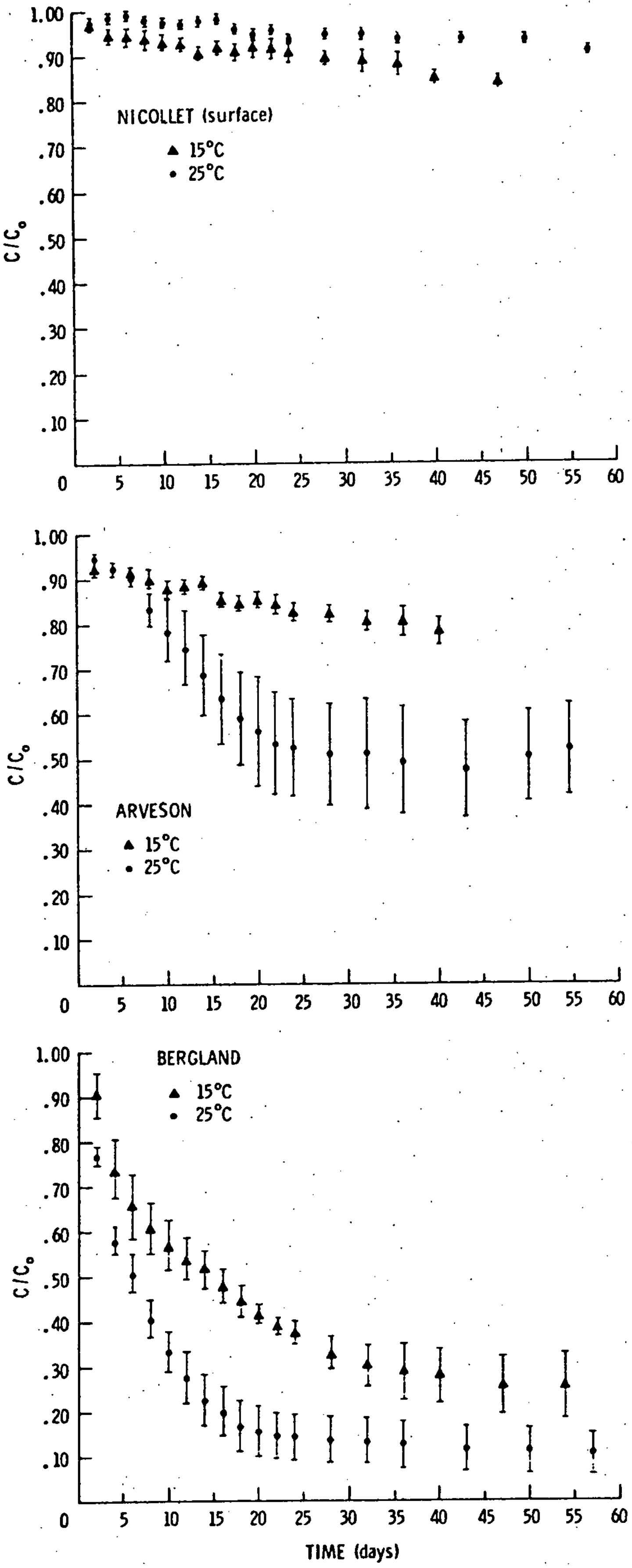


Fig. 9. Effect of aeration by bubbling on ^{99}Tc sorption by Nicollet, Arveson and Bergland soils from aqueous solution at 15 and 25^{o}C. Values are means of triplicate samples with standard errors of the means indicated by the brackets.

soils (Fig. 9). Also, there was greater sorption at 15°C than 25°C indicating that a different process may be involved.

Sorption of ^{99}Tc by different samples of the same soil type: Earlier results showing that under aerated conditions at 25°C, Bergland surface soil was much more effective in sorbing ^{99}Tc from aqueous solution than was Nicollet surface soil could not be clearly related to any measured or known differences in chemical or physical properties of the 2 soils. As a result, 4 additional samples of each soil were collected from different sites, characterized in terms of several chemical and physical characteristics and used in similar ^{99}Tc sorption experiments to determine 1) whether the earlier results were typical for all samples of each soil type, and 2) whether any observed differences in ^{99}Tc sorption behavior between samples of a given soil type could be related to differences in the chemical or physical characteristics of the soils.

Sorption results, expressed as the fraction of ^{99}Tc originally in solution, C/C_o vs. time, showed that all Nicollet surface soil samples sorbed 10% or less of the ^{99}Tc from solution over a period of 2 to 3 weeks (Fig. 10) which is consistent with earlier results for aerated soil suspensions. In contrast, all Bergland samples showed significantly greater ^{99}Tc sorption than the Nicollet soils over the same period. However, there were differences between the sorption rates for the different samples of Bergland soil; i.e. sorption rates were greater for samples 2 and 4 compared to samples 1 and 3.

An examination of the physical and chemical properties of these samples (Table 4) show that the Nicollet samples are all very similar which may explain their similar sorption behavior. Samples 2 and 4 of the Bergland soil were also quite similar in terms of pH, clay content and organic carbon. Sample 3 differed in that it had a somewhat lower

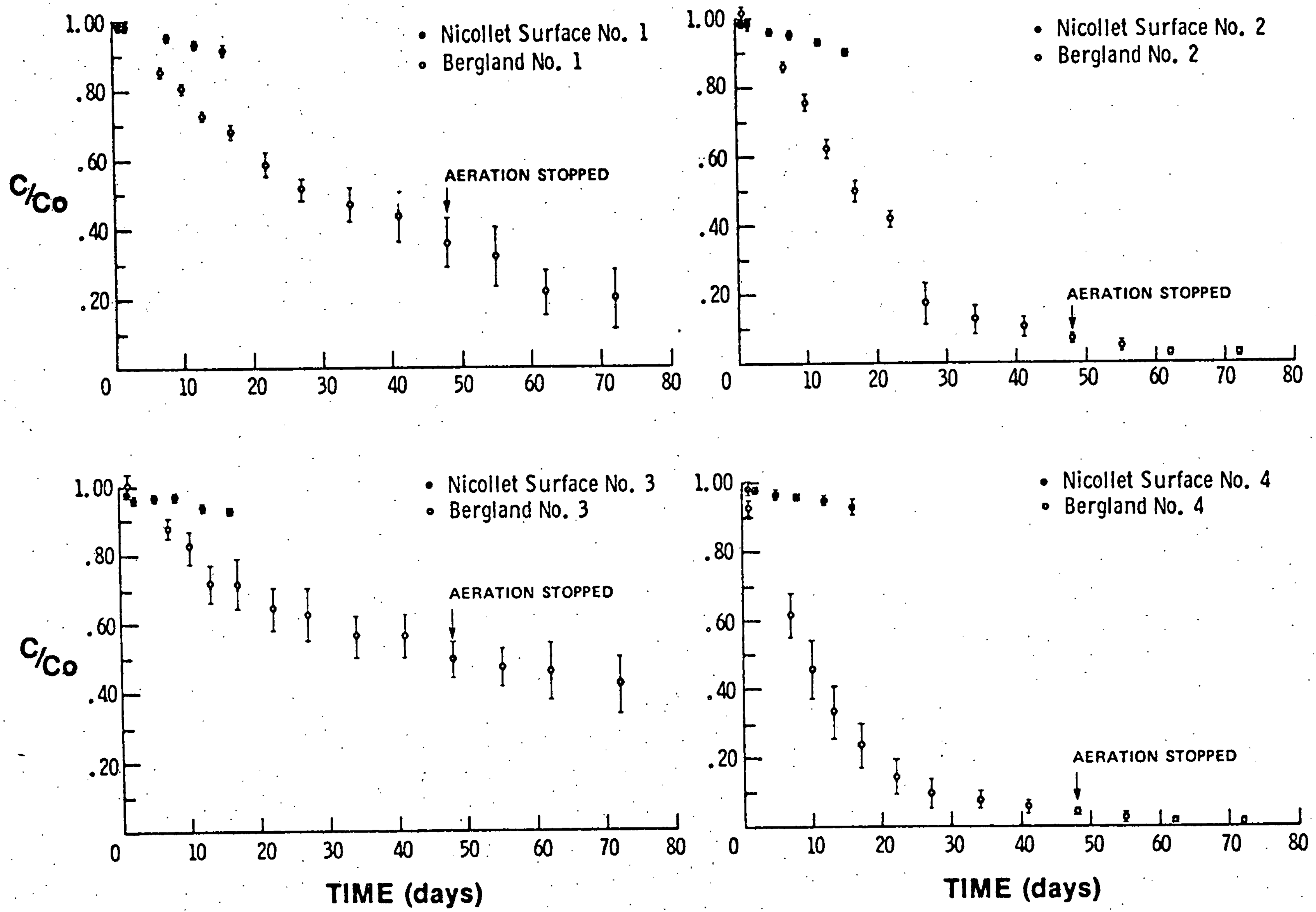


Fig. 10. Technetium-99 sorption at 25°C by four samples of Nicollet and Bergland surface soils plotted as the fraction of ^{99}Tc, C/Co, remaining in solution as a function of time. Values are the means of triplicate samples with standard errors of the means indicated by brackets.

Table 4. Chemical and physical characteristics of five samples of Nicollet and Bergland surface soils taken at different locations.

Soil	pH (H$_2$O)	pH (KCl)	Texture % Sand	Texture % Silt	Texture % Clay	% Org. C	% Fe$_2$O$_3$
Nicollet - orig.*	5.9	4.8	32.3	48.0	24.3	2.3	1.18
" - 1	7.0	5.9	43.3	31.5	25.2	1.5	1.62
" - 2	5.5	4.7	38.1	35.7	26.2	2.6	1.62
" - 3	6.1	5.1	41.0	32.1	27.0	2.1	1.19
" - 4	7.4	6.4	33.6	39.2	27.2	2.6	1.05
Bergland - orig.*	6.2	5.4	20.2	26.0	53.9	4.8	3.00
" - 1	5.8	4.8	8.7	51.5	39.8	7.3	2.06
" - 2	5.9	4.9	15.8	43.5	61.5	8.5	2.30
" - 3	5.4	4.1	2.8	20.7	76.5	4.7	3.09
" - 4	6.1	5.0	3.9	24.0	72.1	9.3	1.66

* Original soil samples used

carbon content, a high clay content and a higher free iron oxide content. In contrast, sample 1 had a low clay content and a high carbon content.

While these results do give some indication that the ^{99}Tc sorption properties are related to differences in their chemical and physical properties, the sorption mechanisms are still far from clear. As shown earlier, sterilization of the Bergland soil eliminated its ^{99}Tc sorption property. While these studies were conducted in closed containers compared to the aerated systems used here, the results do indicate that a microbial process is in some way involved. However, it seems highly unlikely that the microbial population would be greatly different between the Nicollet and Bergland soils, much less between four samples of Bergland soil sampled in the same geographical area.

Effects of inoculation, dextrose addition and incubation on sorption of ^{99}Tc: Inoculation of the previously non-sorbing Nicollet subsurface soil with 1% of Nicollet surface soil, had relatively little, if any effect on the sorption of ^{99}Tc by the subsurface soil regardless of the degree of aeration or incubation (Figs. 11, 12, 13, 14). In contrast, the addition of dextrose resulted in significant sorption of ^{99}Tc by the subsurface soil both with and without aeration and/or incubation. In addition, the rate of ^{99}Tc sorption increased with increasing levels of dextrose addition (Figs. 11 and 13) and was generally greater under anaerobic (closed bottle) conditions than under aerobic (bubbling) conditions for a given level of dextrose. Also the kinetics of ^{99}Tc sorption increased when soils inoculated with dextrose were first incubated than soils with no incubation period.

These results along with the observation that the addition of dextrose alone without prior inoculation with surface soil resulted in sorption all point toward a close relationship between ^{99}Tc sorption and microbial

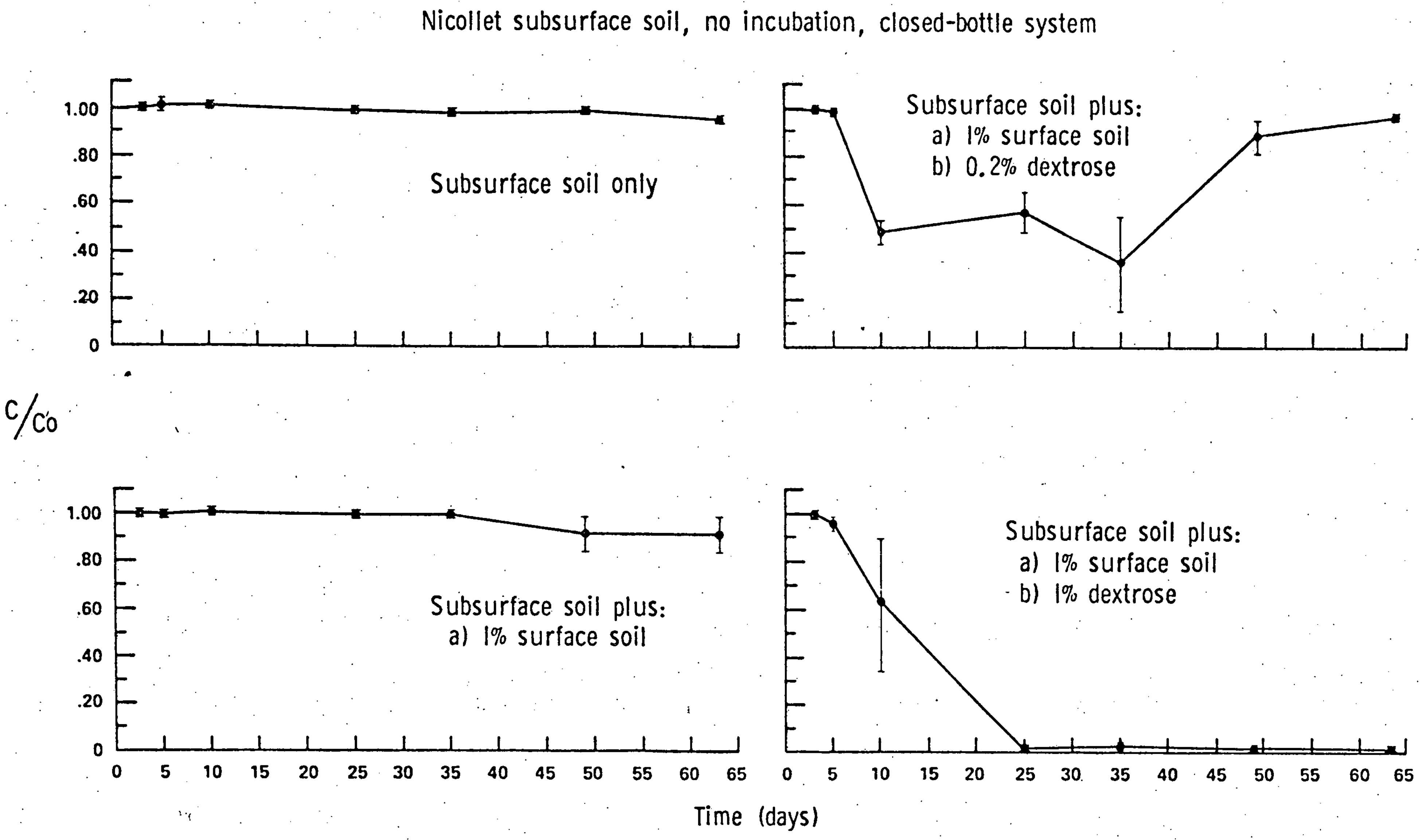


Fig. 11. Effect of dextrose addition to Nicollet subsurface soil, with no incubation, on ^{99}Tc sorption in a closed bottle system. The points plotted represent the means of duplicate samples with standard errors indicated by brackets.

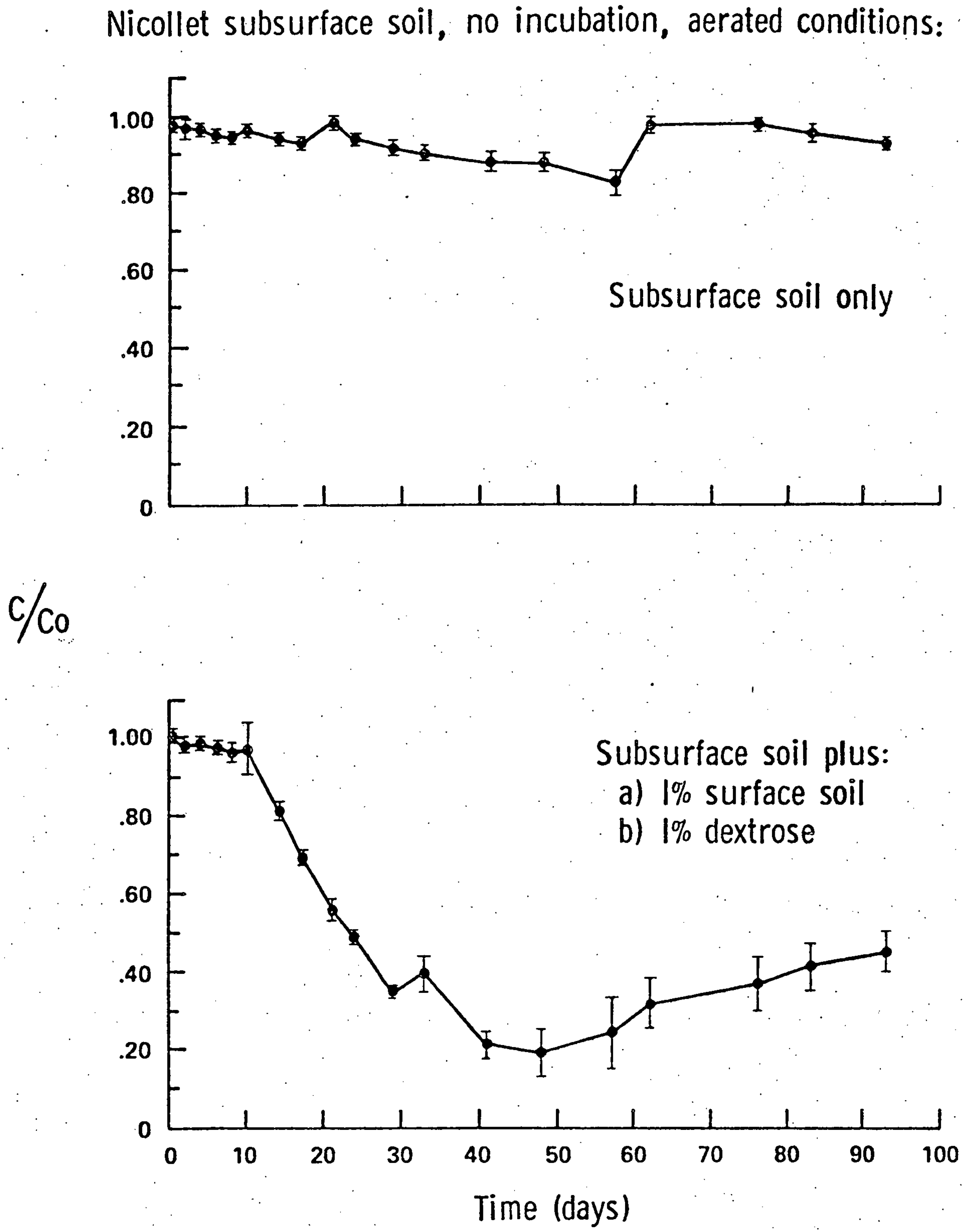


Fig. 12. Effect of dextrose addition to Nicollet subsurface soil, with no incubation, on ^{99}Tc sorption under aerated conditions. The points plotted represent the means of triplicate samples with standard errors indicated by brackets.

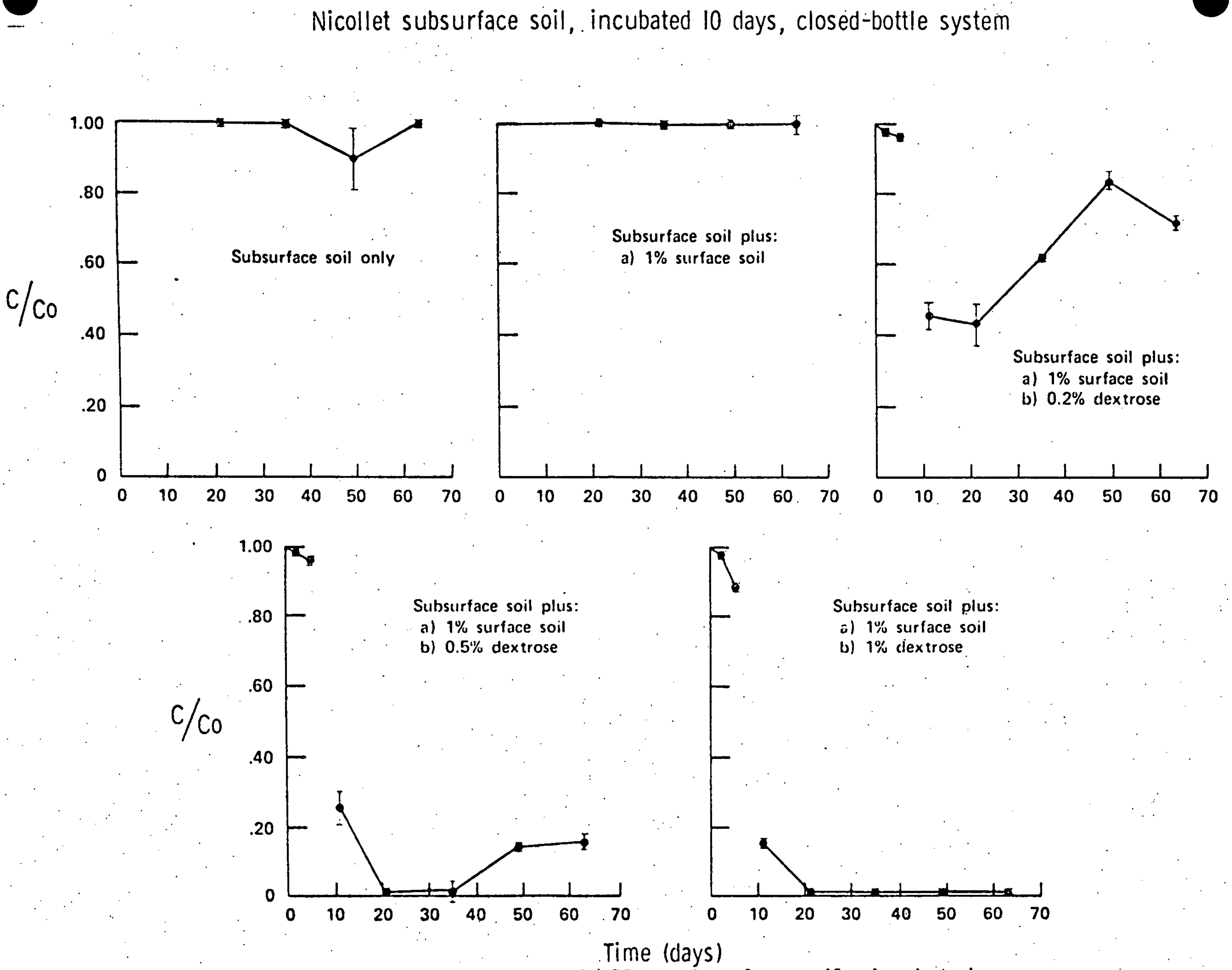


Fig. 13. Effect of dextrose addition to Nicollet subsurface soil, incubated for 10 days, on ^{99}Tc sorption in a closed bottle system. The points plotted represent the means of duplicate samples with standard errors indicated by brackets.

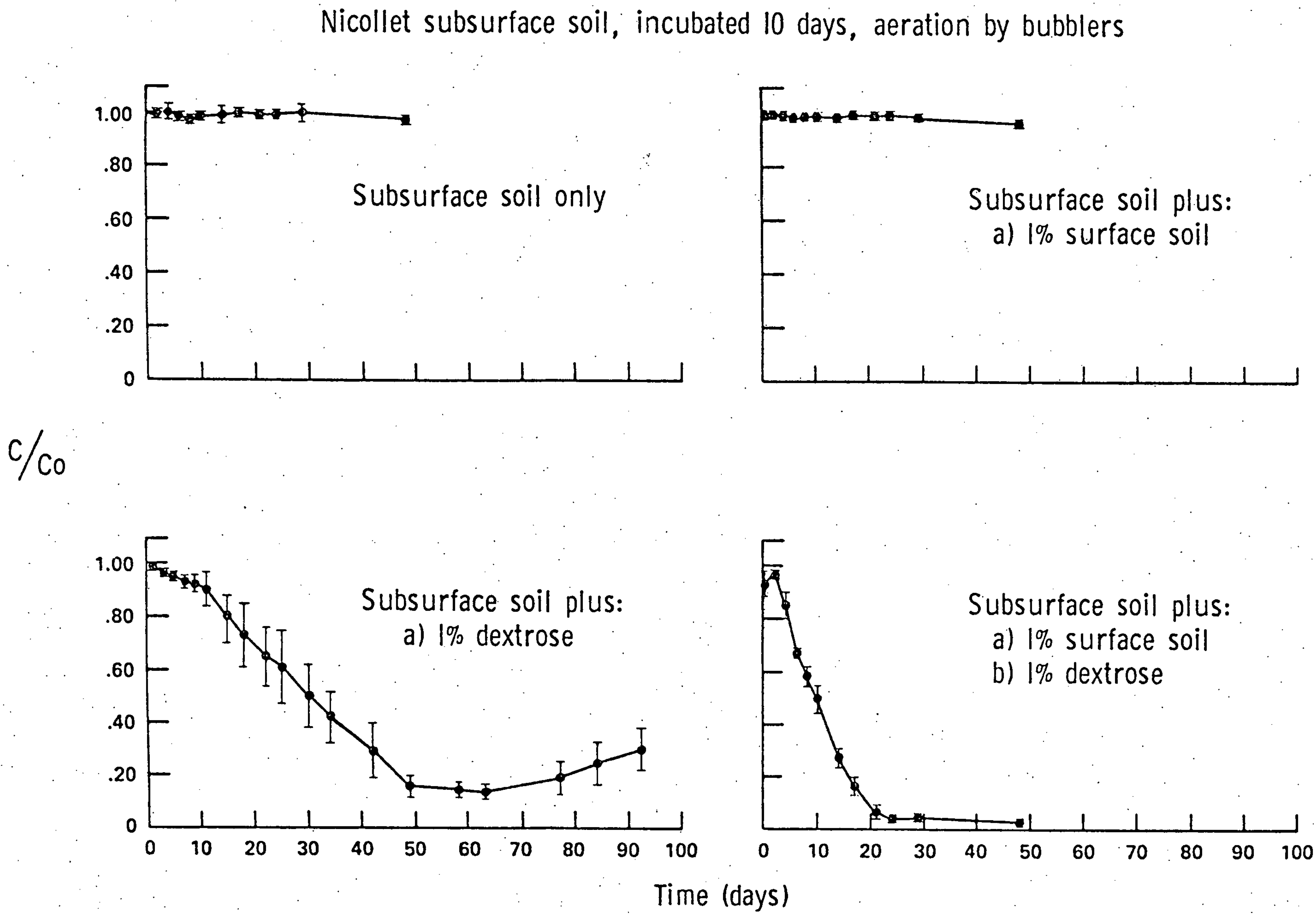


Fig. 14. Effect of dextrose addition to Nicollet subsurface soil, incubated for 10 days, on ^{99}Tc sorption under aerated conditions. The points plotted represent the means of triplicate samples with standard errors indicated by brackets.

activity and that the lack of an energy source is apparently the limiting factor in the non-sorbing Nicollet soil rather than a lack of the necessary microbial population.

Effect of methiolate on ^{99}Tc sorption by soil: As in the case of steam sterilization shown earlier (Fig. 6), the addition of 0.01% methiolate eliminated ^{99}Tc sorption in the previously sorbing Nicollet subsurface soil plus 1% dextrose system (Fig. 15). The soil receiving the additional 1% dextrose dose showed very little increase in the kinetics of ^{99}Tc sorption (Fig. 15). This again indicates that microbial activity is either directly or indirectly involved in the sorption process.

Plant Uptake of ^{99}Tc:

Uptake from simple solution: Results of the solution uptake experiments (Table 5) show that significant amounts of ^{99}Tc can cross the solution/root interface and be translocated into the photosynthetic tissue of all the crops studied. Uptake from distilled water and 0.5 mM $CaCl_2$ showed essentially the same patterns indicating that plant uptake of ^{99}Tc is not greatly affected by the presence of minimal amounts of free salts. The most apparent difference between crops is the high root/shoot concentration ratio found for the dicotyledon species (radishes and soybeans) as compared to that for the monocots (corn, oats, barley and wheat) indicating that significant physiological differences may exist between plant species.

Uptake from irrigated soils: Plant uptake from unfertilized, irrigated soils (Table 6) show between 42 and 67% of the applied ^{99}Tc in the aerial tissue of the wheat seedlings. Results of the solution uptake studies (Table 5) indicate that another 5 to 7% of the applied activity may be in the root tissue. Apparently, any interaction that may have occurred between the ^{99}Tc and the soil during the relatively

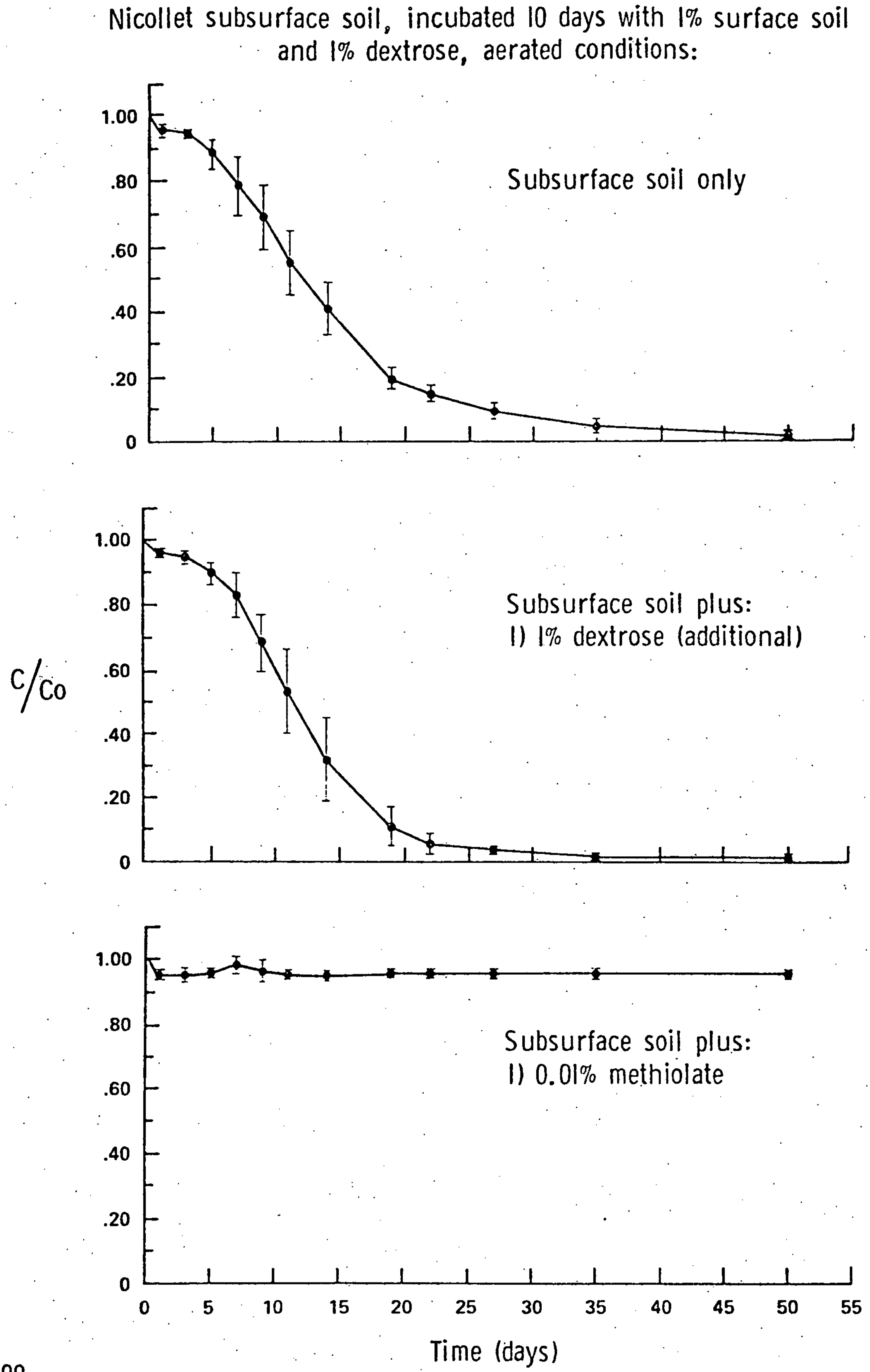


Fig. 15. ^{99}Tc sorption from Nicollet subsurface soil, under aerated conditions, treated with either dextrose or methiolate after a 10 day incubation period in the presence of 1% dextrose. The points plotted represent the means of triplicate samples with standard errors indicated by brackets.

Table 5. Plant uptake of ^{99}Tc from distilled water and 0.5 mM $CaCl_2$. Tabulated values are means of three replicates with standard errors of the means indicated in parentheses.

Plant Species and Segments		% added Tc-99 in segment		µCi Tc-99 per g tissue*		Root/Shoot conc. ratio**	
		dist. H_2O	0.5 mM $CaCl_2$	dist. H_2O	0.5 mM $CaCl_2$	dist. H_2O	0.5 mM $CaCl_2$
Wheat	shoot	18(2.4)	11(2.6)	1.44(0.17)	1.04(0.07)	0.11(0.006)	0.12(0.008)
	root	2(0.3)	2(0.3)	0.16(0.02)	0.13(0.01)		
Barley	shoot	18(3.8)	9(2.0)	1.00(0.21)	0.54(0.07)	0.16(0.06)	0.15(0.003)
	root	2(0.3)	1(0.2)	0.13(0.02)	0.08(0.01)		
Oats	shoot	9(0.8)	6(0.2)	0.57(0.04)	0.51(0.05)	0.20(0.03)	0.16(0.01)
	root	2(0.3)	1(0.1)	0.12(0.03)	0.08(0.01)		
Radish	shoot	23(2.1)	30(9.3)	0.85(0.07)	1.11(0.29)	1.33(0.09)	0.85(0.17)
	root	9(0.6)	7(1.3)	1.12(0.05)	0.85(0.11)		
Soybean	shoot	58(1.8)	63(5.7)	1.67(0.14)	2.12(0.07)	0.51(0.06)	0.43(0.05)
	root	15(0.8)	13(0.6)	0.84(0.03)	0.91(0.10)		
Corn	shoot	30(6.4)	20(2.4)	0.61(0.09)	0.57(0.12)	0.22(0.02)	0.20(0.06)
	root	8(1.8)	5(0.1)	0.14(0.03)	0.10(0.01)		

* concentration factors $\left(\frac{\mu Ci/g\ tissue}{\mu Ci/g\ solution}\right)$ can be obtained by multiplying tabulated values by 50.

** root/shoot concentration ratio = $\frac{(\mu Ci/g)root}{(\mu Ci/g)shoot}$

Table 6. Uptake of ^{99}Tc by aerial parts of wheat seedlings from unfertilized and fertilized soils irrigated with ^{99}Tc labeled water. Tabulated values are means of 3 replicates with standard errors of the means indicated in parentheses.

Soil	Tissue dry weight (mg)		% of added Tc-99 in aerial tissue		Tc-99 concentration in plant tissue[+‡] (μCi/g)	
	unfert.	fert.	unfert.	fert.	unfert.	fert.
Bearden	231(12)	225(8)	64(2.2)	35(3.4)	16.6 bcd**	9.2 c
Hegne	165(5)	191(6)	61(0.1)	49(1.6)	22.4 ef**	15.2 fg
Hibbing	201(14)	235(9)	62(2.6)	56(1.4)	18.5 cde**	14.3 efg
Nicollet (surface)	169(12)	179(2)	67(0.8)	52(4.7)	24.0 f*	17.5 gh
Nicollet (subsurface)	161(7)	186(3)	57(2.2)	62(3.2)	21.3 ef	19.9 h
Omega	193(6)	211(8)	42(0.1)	31(3.5)	13.1 ab*	8.9 bc
Bergland	195(4)	207(0.1)	62(1.2)	54(0.6)	19.1 de**	16.0 fg
Arveson	191(2)	206(5)	44(2.8)	17(0.6)	13.7 ab**	5.0 a
Waukegan	144(13)	204(6)	56(4.4)	59(5.0)	23.2 f**	17.5 gh
Zimmerman	147(9)	171(5)	52(2.3)	47(1.4)	21.1 ef**	16.5 fgh
peat	275(4)	350(25)	54(3.0)	77(2.3)	11.8 a	13.2 def

[+] Concentration factors, $\left(\frac{\mu Ci/g\ tissue}{\mu Ci/g\ soil}\right)$, can be obtained by multiplying (μCi/g) by 50.

[‡] Means in same column followed by same letter are not significantly different at the 5% level by Tukey's test (Steel and Torrie, 1960).

*,** Tissue concentration means for unfertilized vs. fertilized treatments (for a given soil) significantly different at the 5% and 1% level of probability respectively.

short contact period in these studies had relatively little effect on its availability for plant uptake. These results are consistent with those reported earlier in this report which show that soil sorption periods of from 2 to 6 weeks may be required to reach equilibrium ^{99}Tc concentrations in soil-water systems with considerable variation in the amount of sorption between soils and with different experimental conditions.

Application of N-P-K reduced the tissue concentration of ^{99}Tc in all but the Nicollet subsurface- and peat-grown seedlings. Plants grown in both the true solutions and irrigated soils appeared to have normal growth characteristics.

Uptake from incubated soils: Plants germinated and grown in soils which had been moist incubated with ^{99}Tc for 2 months generally showed severe growth reduction compared to those for the irrigated soils as evidenced by both visual observation and final tissue dry weights (Tables 6 and 7). Even though yields from the incubation and irrigation studies are not directly comparable due to differences in harvest times, this, alone cannot account for the large differences in tissue weight. While the seeds had germinated and emerged by the fifth day after planting, the first leaf failed to grow out of the coleoptile on many of the plants. Dessication and death soon followed on such plants. Leaves of the surviving plants were often very dark green with some yellowing of the tips, and displayed a twisted and stunted growth habit.

Since most of the soils showed signs of fungal growth at the end of the 2 month moist incubation period, it was thought that the poor plant growth might be due to a plant pathogen. However, macroscopic examination of the seedlings by plant pathologists failed to reveal any symptoms of infectious disease, and fungicide-seed treatment failed to stimulate growth on similarly incubated soils. The severe stunting observed also suggested that a nutrient deficiency might be responsible

Table 7. Uptake of ^{99}Tc of aerial parts of wheat seedlings from unfertilized and fertilized soils moist-incubated with ^{99}Tc for two months prior to seeding. Tabulated values are means of three replicates with standard errors of the means indicated in parentheses.

Soil	Tissue dry weight (mg)		% of added Tc-99 in aerial tissue		Tc-99 concentration in plant tissue[+][‡] (μCi/g)	
	unfert.	fert.	unfert.	fert.	unfert.	fert.
Bearden	54(6)	249(11)	17(1.4)	8(2.0)	19.4 bcd	1.9 a
Hegne	30(2)	119(6)	7(0.3)	7(0.9)	14.2 abc	3.8 ab
Hibbing	43(13)	170(5)	15(4.4)	22(3.7)	29.8 e	7.0 abc
Nicollet (surface)	32(2)	96(18)	14(2.0)	22(3.9)	25.5 de	14.1 cd
Nicollet (subsurface)	10(0.4)	26(7)	5(0.6)	11(2.3)	26.2 de	26.1 e
Omega	105(26)	159(7)	12(4.5)	12.4(1.3)	5.9 a	4.7 abc
Bergland	55(6)	141(11)	13(1.2)	23(2.7)	14.4 abc	10.1 abcd
Arveson	72(12)	177(15)	12(3.4)	21(1.6)	10.5 ab	7.0 abc
Waukegan	17(3)	27(5)	7(1.2)	8(1.4)	23.4 cde	17.7 de
Zimmerman	18(3)	121(13)	5(0.3)	23(4.1)	16.1 abcd	11.9 bcd
peat	28(5)	64(8)	7(0.7)	18(2.8)	14.3 abc	17.2 de

[+] Concentration factors, $\left(\frac{\mu Ci/g\ tissue}{\mu Ci/g\ soil}\right)$, can be obtained by multiplying (μCi/g) by 50.

[‡] Means in same column followed by same letter are not significantly different at the 5% level by Tukey's test (Steel and Torrie, 1960).

for poor growth, perhaps due to microbial immobilization of essential elements during incubation. However, irrigation with 1/10 strength Hoagland solution failed to stimulate growth, indicating this is not the case.

While plant growth in the incubated soils was poor in most cases, the ^{99}Tc tissue concentrations are in general quite similar to those found in the irrigation studies (Table 6). This would not be expected from the results of soil sorption experiments reported earlier unless either (1) sorbed technetium is readily plant-available, or (2) the incubated soil system is not analogous to the earlier soil sorption systems studied and the ^{99}Tc remains unsorbed.

Since 0.01 $\underline{M}$ $CaCl_2$ is said to approximate the total electrolyte concentration in the soil solution of non-saline soils at optimum field water content (Peech, 1965), it was used as an extracting agent to test for non-sorbed ^{99}Tc. Overnight shaking of Bearden, Hibbing and Waukegan soil samples, which had sorbed 88% or more of added ^{99}Tc in previous laboratory experiments, resulted in 11% or less of the sorbed fraction being released to the 0.01 $\underline{M}$ $CaCl_2$ solution. Thus, as 0.01 $\underline{M}$ $CaCl_2$ is a poor extractant of sorbed ^{99}Tc, it should give some indication of the quantity of free, non-sorbed ^{99}Tc present in a soil sample. Therefore, a single pot of each of the unfertilized, incubated soils was sampled, extracted overnight with $CaCl_2$ (1:3 soil:$CaCl_2$ by wt.) and the solution assayed for ^{99}Tc. The results (Table 8) indicate that a large percent of the applied ^{99}Tc is still "free" after 2 months of moist incubation. Thus, the high plant ^{99}Tc tissue concentrations observed are not inconsistent with those from the irrigation study. While the high $CaCl_2$ extraction figures appear to agree with the high tissue concentrations observed, the linear regression correlation coefficient between the two

Table 8. Extraction of ^{99}Tc from moist-incubated soils by 0.01 M $CaCl_2$. Tabulated values are means of triplicate samples with standard errors of the means indicated in parentheses.

Soil	Percent Extractable
Bearden	70 (3.8)
Hegne	72 (1.1)
Hibbing	79 (2.4)
Nicollet (surface)	78 (2.7)
Nicollet (subsurface)	101 (2.9)
Omega	31 (1.4)
Bergland	67 (0.3)
Arveson	79 (3.2)
Waukegan	84 (2.2)
Zimmerman	62 (1.9)
Peat	100 (7.9)

parameters was only 0.58 . The reason for the high percentage of non-sorbed ^{99}Tc after 2 months of soil contact is not clear, but may be related to aeration effects.

Effect of ^{99}Tc on germinating seeds and young seedlings: Yield results for the 6 crop species germinated and grown for 10 days in solutions containing increasing amounts of ^{99}Tc show that all are sensitive to low concentrations of ^{99}Tc (Figs. 16 and 17). Corn and soybeans showed a significant yield increase ($p < 0.001$) on the first ^{99}Tc addition indicating a possible stimulation effect. Greatest yield reduction in both shoot and root tissue of the three small grains and radishes occurred between initial solution concentrations of 0 to 2.5 μCi ^{99}Tc/50 ml (0-2.8 μg Tc/ml) (Fig. 16). Soybeans and corn behaved somewhat differently in that the greatest yield reductions appeared beyond initial solution concentrations of 2.5 μCi ^{99}Tc/50 ml (Fig. 17).

Results for the experiment in which wheat seedlings were germinated and grown for 10 days in 50 ml of Hoagland solution containing initial ^{99}Tc concentrations of 0-1.0 μCi/50 ml are shown in Fig. 18, identified as P-10. There was an initial yield reduction following the ^{99}Tc addition of 0.0125 μCi/50 ml (0.014 μg Tc/ml), variable results for additions between 0.0125 and 0.25 μCi/ml and a general decline in yield for ^{99}Tc additions beyond this point. Results for wheat seedlings from the experiment shown in Fig. 16 (identified as P-8) and from an earlier experiment (Landa et al., 1977) (identified as P-7) are also shown in Fig. 18 for comparison purposes. While there may be some question as to whether there is a "threshold level" between additions of 0 and 0.25 μCi/50 ml, the overall results suggest that ^{99}Tc is progressively toxic with increasing concentration.

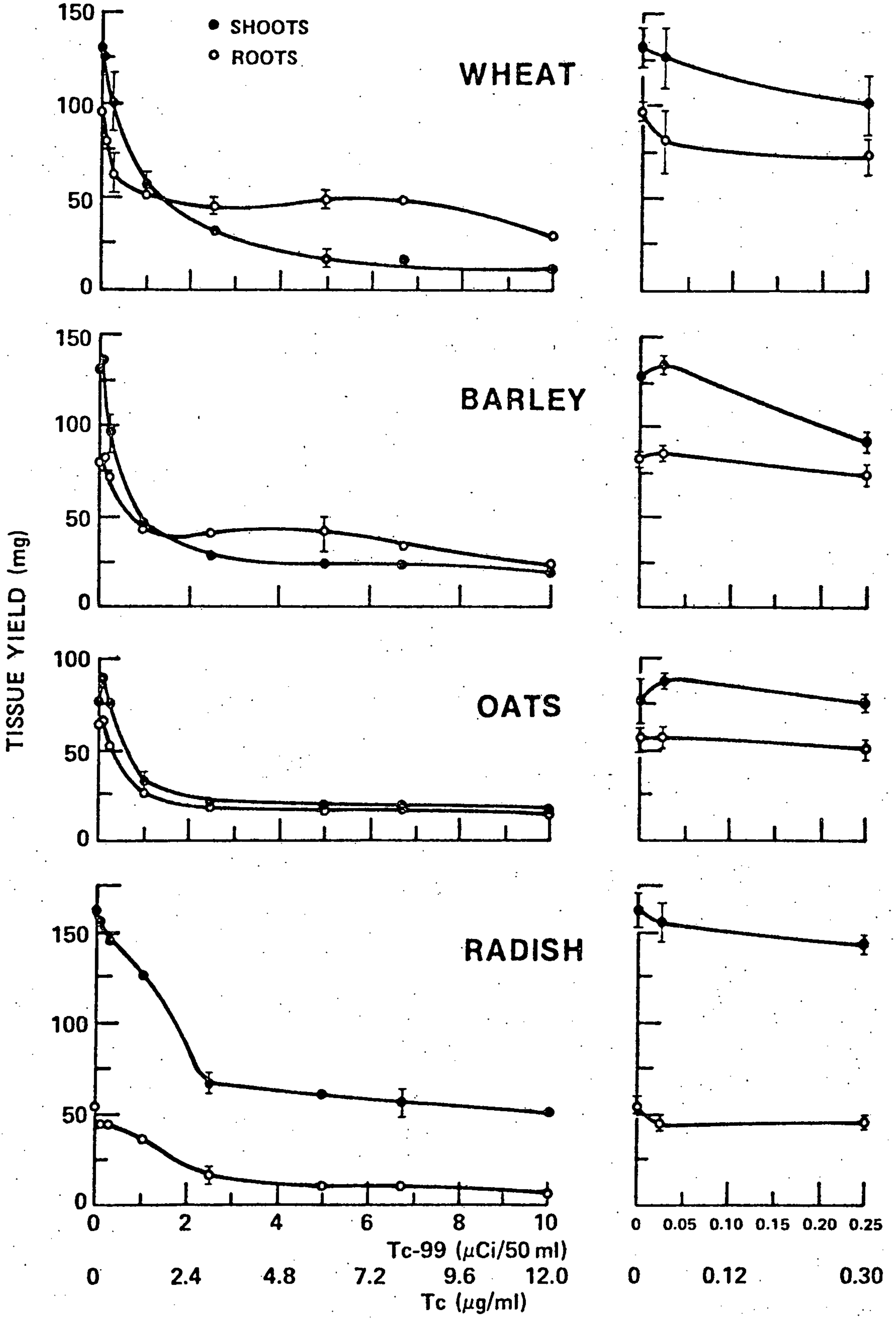


Fig. 16. Tissue yield of 10-day-old wheat, barley, oat and radish seedlings germinated and grown in 50 ml of 1/3 strength Hoagland solution containing increasing amounts of ^{99}Tc. Values are means of duplicate samples with standard errors of the means indicated by brackets.

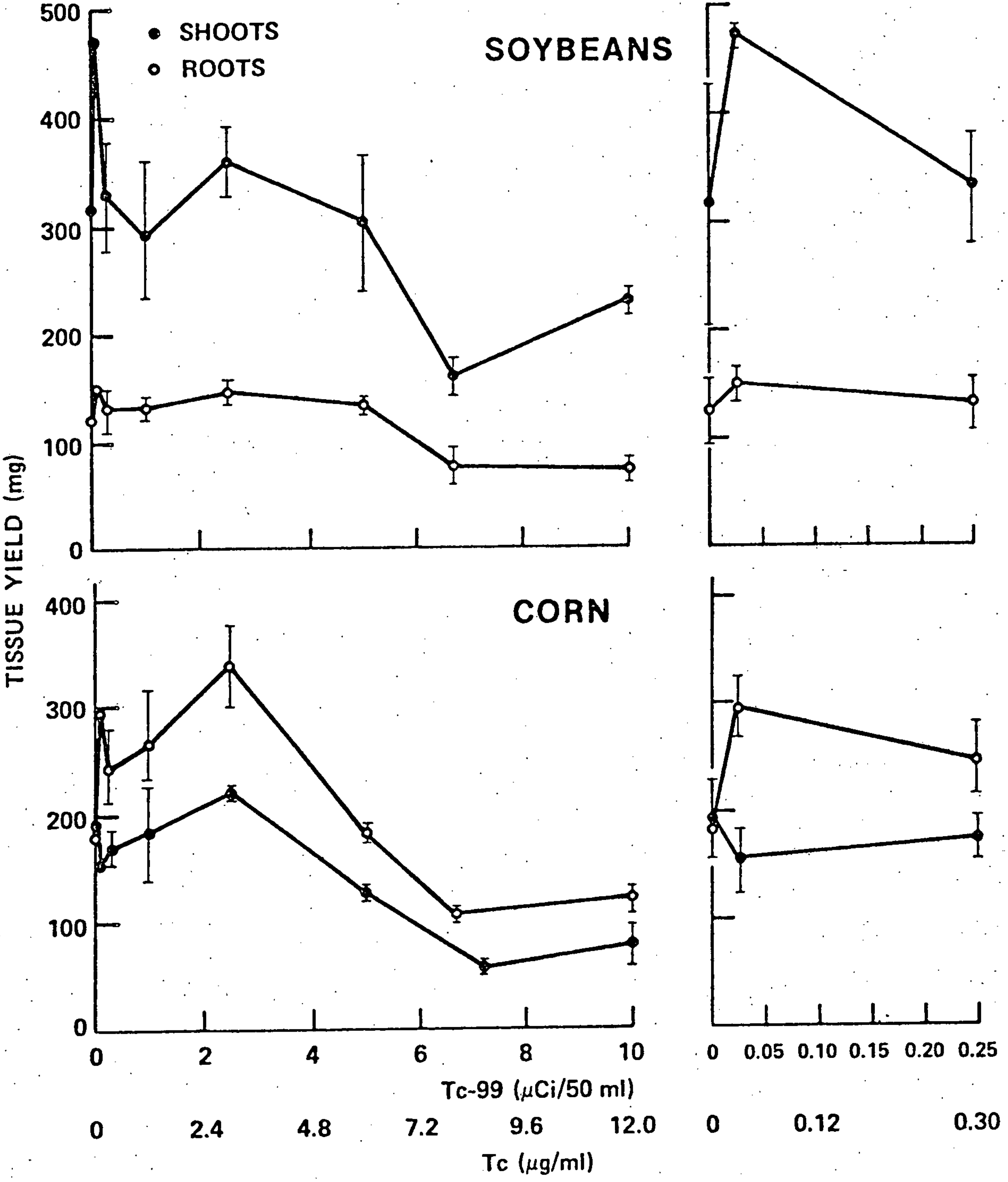


Fig. 17. Tissue yield of 10-day-old soybean and corn seedlings germinated and grown in 50 ml of 1/3 strength Hoagland solution containing increasing amounts of ^{99}Tc. Values are means of duplicate samples with standard errors of the means indicated by brackets.

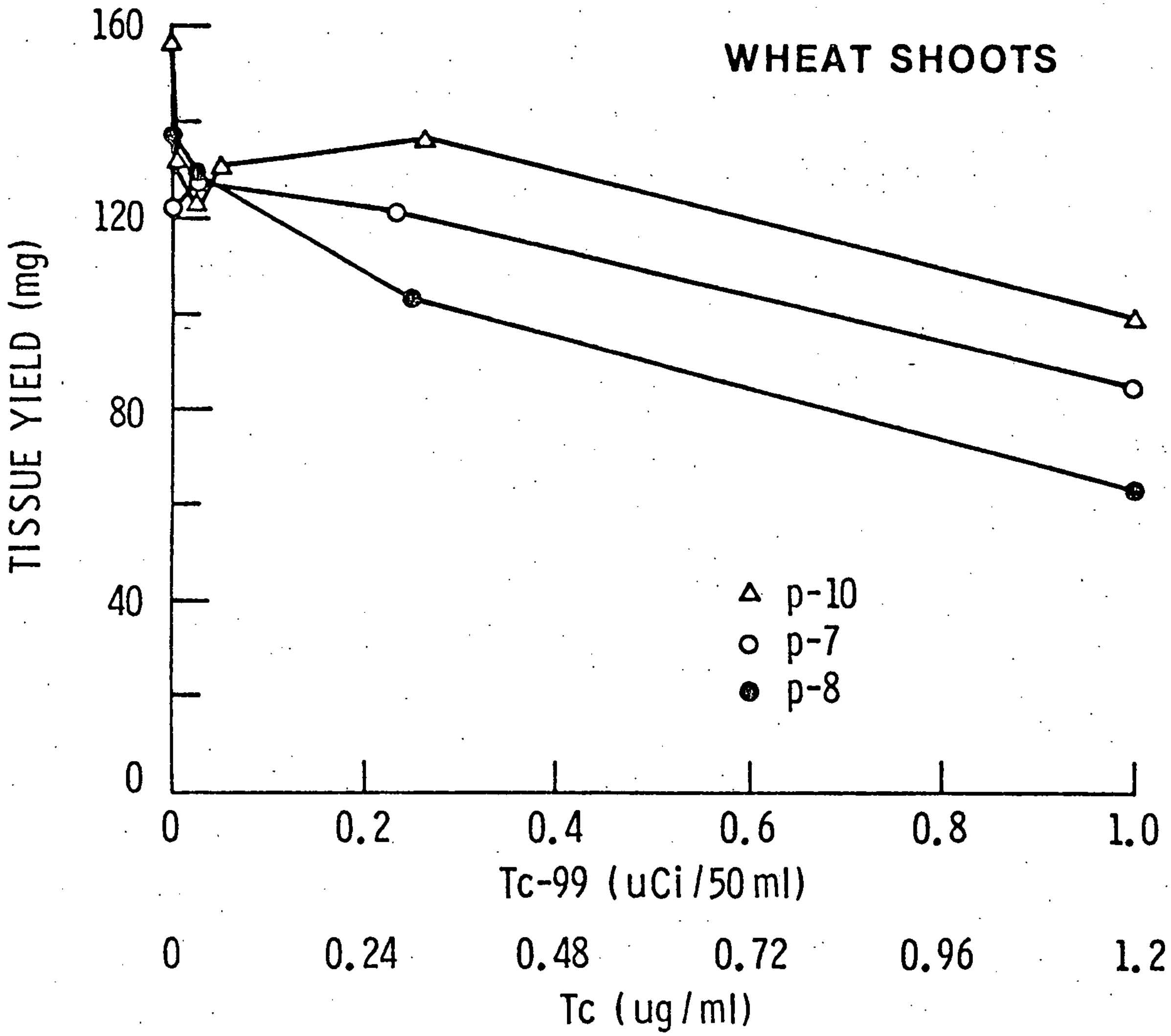


Fig. 18. Tissue yield of 10-day-old wheat seedlings grown in 50 ml of 1/3 strength Hoagland solution containing increasing amounts of ^{99}Tc. Results are for three different experiments.

Technetium-99 concentrations in shoot and root tissue of the plants whose yields are shown in Figs. 16 and 17 increased with additions up to 6.7 μCi/50 ml (Tables 9 and 10). Increasing the ^{99}Tc addition to 10.0 μCi/50 ml resulted in a continued increase in tissue concentration in some instances and either little change or a decrease in others. Shoot tissue concentrations in wheat, barley, oats and radishes at the 2.5 μCi ^{99}Tc/50 ml level ranged from 9.0 to 19.6 μCi ^{99}Tc/g tissue or 523 to 10,248 μg Tc/g tissue; i.e. μg Tc/g tissue = (μCi ^{99}Tc/g tissue) x (58.1). By comparison, concentrations in the shoot tissue of soybeans and corn at the same level of ^{99}Tc addition were 2.3 and 3.8 μCi ^{99}Tc/g or 134 and 221 μg Tc/g, respectively. These differences in tissue concentration may well account for the relative differences in response of the small grains and radishes (Fig. 16) vs. soybeans and corn (Fig. 17) to the levels of ^{99}Tc addition in the growth media; i.e. even though there was a greater total ^{99}Tc uptake by the shoots of soybeans and corn (0.83 and 0.84 μCi, respectively) compared to wheat and barley (0.34 and 0.38 μCi, respectively), the tissue concentration was significantly less in the case of soybeans and corn due to greater total dry matter production. In the case of radishes, there was both a greater ^{99}Tc concentration and greater total growth resulting in a greater total ^{99}Tc uptake of 1.32 μCi. The root/shoot concentration ratios tended to increase with increasing ^{99}Tc additions for the small grains while values for corn were somewhat variable (Table 10). Roots rinsed with running deionized water as compared to washing with .5 mM $CaCl_2$ showed no significant difference in results ($p > .50$) indicating that the ^{99}Tc was not sorbed on the root surface.

Table 9. Technetium-99 concentration in shoot tissue of 10-day-old seedlings of 6 crop species germinated and grown in 50 ml of 1/3 strength Hoagland solution containing increasing amounts of ^{99}Tc.*

^{99}Tc soln conc.		Wheat	Barley	Oats	Radish	Soybeans	Corn
µCi / 50ml	µg Tc / ml	^{99}Tc (µCi/g)	^{99}Tc (µCi/g)	^{99}Tc (µCi/g)	^{99}Tc (µCi/g)	^{99}Tc (µCi/g)	^{99}Tc (µCi/g)
Control		0	0	0	0	0	0
0.025	0.03	0.07	0.10	0.13	0.12	0.03	0.05
0.25	0.3	0.96	1.04	1.12	1.3	0.25	0.66
1.0	1.2	4.9	5.3	5.7	4.6	1.2	1.7
2.5	3.0	9.0	11.4	--	19.6	2.3	3.8
5.0	5.8	13.7	17.2	10.1	37.7	5.9	8.2
6.7	7.8	25.1	14.8	11.6	39.6	6.8	9.4
10.0	11.6	21.5	10.6	13.7	54.0	5.4	7.2

* (µCi ^{99}Tc/g) (58.1) = µg Tc/g

Table 10. Technetium-99 concentration in root tissue, µCi/g, and ^{99}Tc root to shoot concentration ratio, R/S, of 10-day-old seedlings of 6 crop species germinated and grown in 50 ml of 1/3 strength Hoagland solution containing increasing amounts of ^{99}Tc.*

^{99}Tc soln conc.		Wheat		Barley		Oats		Radish		Soybeans		Corn	
µCi 50ml	µg Tc ml	^{99}Tc (µCi/g)	R/S	^{99}Tc (µCi/g)	R/S	^{99}Tc (µCi/g)	R/S	^{99}Tc (µCi/g)	R/S	^{99}Tc (µCi/g)	R/S	^{99}Tc (µCi/g)	R/S
Control		0	0	0	0	0	0	0	0	0	0	0	0
0.025	0.03	0.02	0.21	0.01	0.10	0.05	0.36	0.2	0.12	0.04	1.45	0.03	0.67
0.25	0.3	0.18	0.19	0.13	0.12	0.23	0.21	0.20	0.16	0.25	0.97	0.12	0.18
1.0	1.2	1.3	0.27	1.5	0.29	1.5	0.26	0.55	0.12	1.1	0.99	0.46	0.27
2.5	3.0	4.6	0.52	4.0	0.35	--	--	2.2	0.11	2.4	1.06	1.4	0.37
5.0	5.8	6.5	0.47	9.5	0.55	8.6	0.85	4.8	0.13	4.7	0.79	3.2	0.39
6.7	7.8	8.0	0.32	14.6	0.99	9.2	0.79	4.8	0.12	5.3	0.77	5.2	0.56
10.0	11.6	10.7	0.50	13.1	1.23	12.8	0.94	10.0	0.19	7.1	1.33	5.5	0.76

* (µCi ^{99}Tc/g) (58.1) = µg Tc/g

The ^{99}Tc induced toxicity could be either chemically or radiologically induced. Since technetium does not have a stable isotope, there is no direct means of distinguishing between these two possible mechanisms. One could test for possible radiological effects by using a radionuclide with nuclear properties similar to ^{99}Tc but known not to cause chemical toxicity in the concentration range examined. However, this would require getting the radionuclide into the plant in concentrations, and with macro- and micro-distributions similar to that for ^{99}Tc, and that would be difficult.

Alternately, tissue dose rates were calculated using the following equation (Lapp and Andrews, 1972):

$$\text{Dose rate} = (C_o)\ (\bar{E}_\beta)\ (5.92 \times 10^{-4})\ \text{rad sec}^{-1}$$

Where C_o = radioisotope concentration in tissue, μCi g^{-1}

$\bar{E}_\beta$ = average beta energy of radioisotope, Mev.

^{99}Tc tissue concentrations were expressed on a wet weight basis for these calculations as succulent tissue is being irradiated in the living plants. The average beta energy for ^{99}Tc was taken as 0.1 Mev.

A tissue dose rate of 2 rads/day at the time of harvest was calculated for the 1.0 μCi/50 ml - treatment, where shoot tissue yield depression was first observed. A dose rate of 16 rads/day was calculated for the shoot tissue at the highest level of added ^{99}Tc or 20 μCi/50 ml. Higher or lower dose rates may have been encountered prior to harvest depending upon the relative rates at which technetium accumulated and new tissue production occurred over the period of the experiment.

These dose rates appear to be quite low when compared with those required in other species to produce growth inhibition (Casarett, 1968). Unfortunately, no reports of studies dealing specifically with wheat seedling growth inhibition in response to chronic irradiation were found in the literature. However, a study of the effect of acute x-irradiation of wheat seedlings by Zirkle and Lampe (1938) showed that exposures of about 400-500 R were required to produce a 20% reduction in shoot growth. While Zirkle and Lampe class wheat seedlings as highly radiosensitive, their data makes a 2 rad/day dose rate seem an unlikely cause for the growth reductions observed here.

The above arguments suggest that ^{99}Tc toxicity is chemical rather than radiological in nature. Also, the ^{99}Tc toxicity symptoms resemble those associated with damage by 2,4-D and related selectively translocated herbicides. Such herbicides function as weed control agents by accumulating to toxic levels in the meristematic regions and inducing cell division and enlargement, callus and tumor formation, and tissue crushing. This unregulated growth leads to complete disorganization of the vascular tissues, and thus, lacking the ability to translocate water, salts and metabolites, the plants die. Symptoms of 2,4-D injury include a twisting or bending of stems and leaves, (resulting from differential growth rates in petioles, pulvini, and elongating regions of the stem) and a cessation of growth followed by death of tissues (Crafts and Robbins, 1962).

If ^{99}Tc toxicity is chemical in nature, it might be expected that the symptoms would be similar to those for stable analogs of pertechnetate such as iodiate whose physiological behavior resembles that of TcO_4^-, at least in animals. Lewis and Powers (1941) found about 20% depression in top tissue yields of barley grown in a nutrient solution containing 0.50 ppm added iodine (tissue iodine content was 160 ppm). At 1.0 ppm added iodine, all plants died. Tissue concentrations as low as 6 ppm have resulted in reduced growth. However, the toxicity symptoms described include a general chlorosis, yellow intervenal patches and brown necrotic spots, and are unlike those seen with ^{99}Tc in wheat seedlings.

Based on the earlier yield data for wheat seedlings germinated and grown in the presence of ^{99}Tc to an age of 10 days, we had generally concluded that the period of greatest sensitivity to ^{99}Tc was during germination and very early growth. This conclusion was confirmed by the results obtained when wheat seedlings were again grown for 10 days with either 1 or 5 μCi additions (Fig. 19). Plants grown under the same conditions, but to a total age of 18 days, continued to show greater yield reductions for early ^{99}Tc additions. However, there was a significant yield reduction at the 5 μCi level for the later additions also indicating that seedlings may be sensitive to ^{99}Tc toxicity at later stages of growth than initially thought.

Tissue yield and ^{99}Tc distribution in mature wheat plants: Results of the experiment where wheat plants were grown to maturity on Bergland and Nicollet surface soil-sand mixtures with either 10 or 20 μCi of ^{99}Tc added in either three equal increments on day 7, 17 and 33 or in one increment on day 7 or 33 after planting show the following general results (Table 11).

1. The 20 μCi additions severely altered plant growth characteristics on both soils at all times of addition. Additions of ^{99}Tc in three increments on day 7, 17 and 33 or in one increment on day 7 prevented seed formation, while seed yields were greatly reduced by a single 20 μCi addition on day 33.
2. Addition of 10 μCi resulted in reduced seed production on both soils with the greater reductions at the earlier times of addition.
3. The 10 μCi addition reduced shoot tissue yields on the Nicollet but not the Bergland soil. This difference can probably be related to a lower ^{99}Tc concentration and percent uptake from the Bergland than the Nicollet soil.

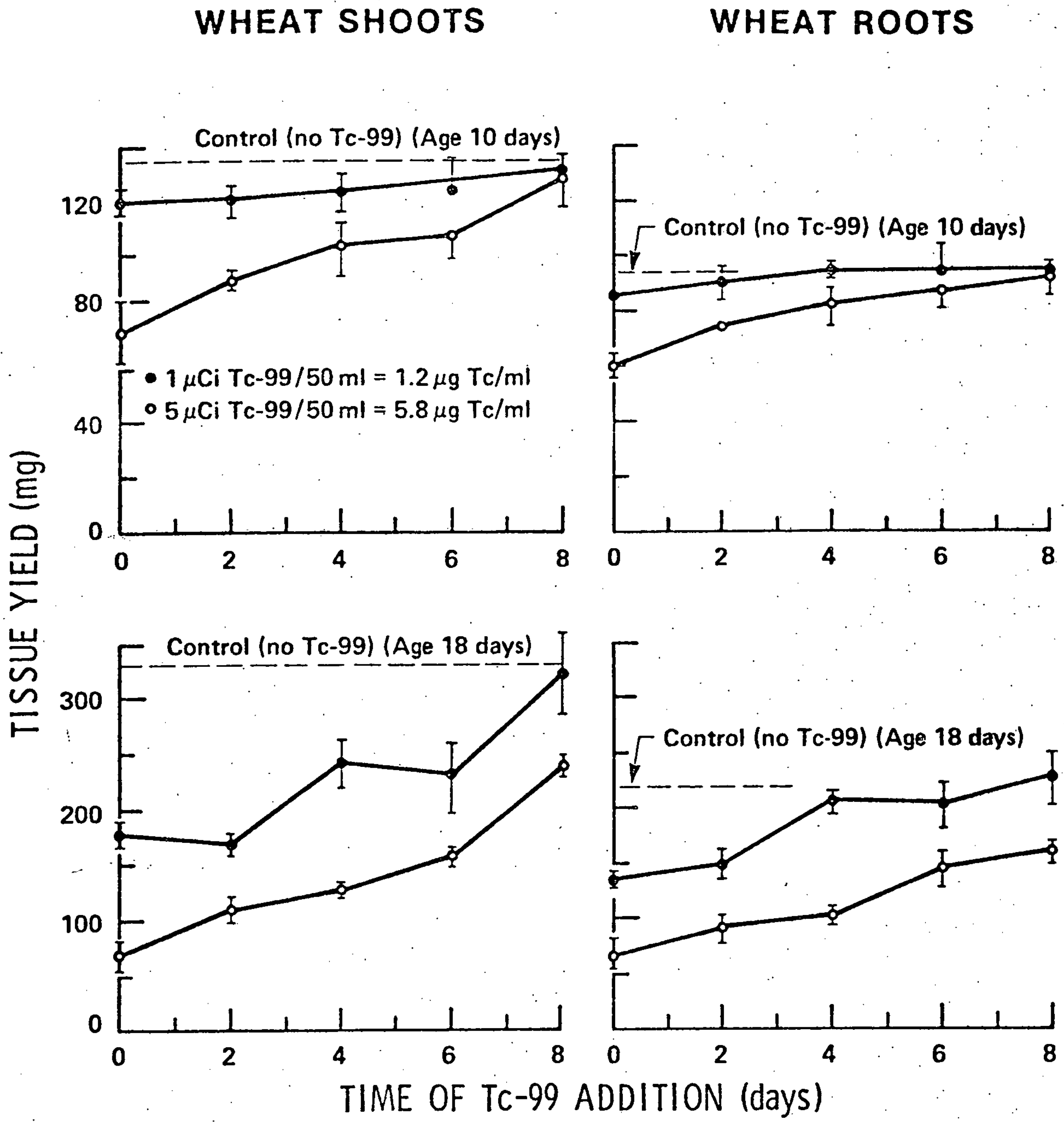


Fig. 19. Tissue yield of 10 and 18 day-old wheat seedlings grown in 50 ml of 1/2 strength Hoagland solution containing either 1.0 or 5.0 μCi of ^{99}Tc added with increasing time after the start of germination. Values aremeans of triplicate samples with standard errors of the means indicated by brackets.

Table 11. Yields and Tc-99 content of mature wheat plants and seeds grown on Nicollet and Bergland surface soils containing 10 or 20 µCi of Tc-99 added at different stages of plant growth. Tabulated values are means of three replicates with standard errors of the mean indicated in parentheses.

Tc-99 added per pot*			Yield		Tc-99 content of plant tissue and seeds					
					1st leaves**		New leaves**		Seeds	
Total added (µCi)	µCi per addition	day of addition	Tops (g)	Seeds (g)	(µCi/g)	(% of added)	(µCi/g)	(% of added)	(µCi/g)	(% of added)
					Nicollet Soil					
Control	0	0	4.02(.16)	0.96(.09)	0	0	0	0	0	0
10	3.33	7,17,33	3.51(.05)	0.28(.04)	2.29(.10)	80.6(3.6)	--	--	0.03(.002)	0.07(.01)
10	10	7	3.16(.03)	0.47(.03)	1.29(.02)	41.1(0.5)	--	--	0.03(.004)	0.15(.02)
10	10	33	2.92(.16)	0.53(.10)	0.48(.01)	13.0(0.1)	--	--	0.01(.001)	0.03(.01)
20	6.67	7,17,33	2.42(.17)	--	3.12(.06)	38.3(0.7)	0.32(.15)	4.1(2.1)	--	--
20	20	7	1.65(.18)	--	2.06(.07)	18.6(0.6)	0.47(.13)	4.1(1.3)	--	--
20	20	33	2.39(.02)	0.03(.03)	7.01(.22)	91.0(2.7)	--	--	--	--
					Bergland Soil					
Control	--	--	3.01(.15)	1.58(.07)	--	--	--	--	--	--
10	3.33	7,17,33	3.16(.13)	0.29(.09)	1.18(.09)	37.3(2.9)	--	--	--	--
10	10	7	3.40(.08)	0.11(.06)	0.63(.02)	22.0(0.6)	--	--	--	--
20	6.67	7,17,33	3.18(.25)	0.41(.09)	--	--	--	--	0.01(.001)	0.02(.002)
20	20	7	1.95(.16)	--	1.61(.07)	14.9(0.6)	0.11(.01)	1.1(.11)	--	--
20	20	33	2.34(.38)	--	5.30(.02)	54.2(0.2)	0.43(.13)	5.0(.54)	--	--
			2.69(.07)	0.08(.06)	--	--	--		0.01(0.001)	0.01(0.00)

* Each greenhouse pot contained 1000 g of 2:1 sand-soil mixture.

** Where data for 1st leaves only is given it represents results for total vegetative tissue.

4. The first (or older) leaves showed much greater ^{99}Tc concentrations than the newer leaves, indicating that ^{99}Tc is not readily translocated from older to newer tissue.
5. ^{99}Tc concentrations in wheat seed was approximately 40 to 80 times less than in vegetative tissue of the plant.

From these results it can generally be concluded that ^{99}Tc can reduce both vegetative growth and seed production even when added at fairly late stages of plant growth and that there is limited transfer of ^{99}Tc to the seeds. The results also suggest that there may be a difference in ^{99}Tc availability between the 2 soils studied, but this will have to be confirmed by further study.

Movement of ^{99}Tc in Minnesota Soils:

Soil Characterization by Soil Column Layer Chromatography: The soils characterized for the sorption study (Tables 1 and 2) were also used for the CLC study of ^{99}Tc movement. Distribution parameters for these 10 mineral soils were determined from each replicate chromatograph column. An additional 15 surface and 16 subsurface soils from Minnesota were also included in the soil CLC study. These mineral soils, with a wide range of physical and chemical properties, were characterized by Pluth et al. (1970) (Tables 12 and 13). The ^{99}Tc distribution for these 31 soils was determined by bulk extraction of the replicate chromatograph column segments.

Distribution of ^{99}Tc in Soil CLC: The distribution of ^{99}Tc in soil CLC plates is defined by three 'R' parameters defined as:

$$R_f = \frac{\text{Distance of front of solute movement}}{\text{Distance of water front movement}}$$

$$R_p = \frac{\text{Distance of peak solute concentration}}{\text{Distance of water front movement}}$$

$$R_b = \frac{\text{Distance of the back of solute movement}}{\text{Distance of water front movement}}$$

where all distances are measured from the point of introduction of the solute. These values, in conjunction with other chromatographic parameters such as K_d, bulk density, and porosity, characterize radionuclide distribution (Table 14, Figure 20-24).

The general trend of R_f indicates that ^{99}Tc moves with the water front under the experimental conditions of aerobic unsaturated flow on the soil CLC plates (Table 14). Using one way analysis of variance and the 'honest significant difference' for sample mean separation, only 8 of the 41 soils tested had R_f significantly different than unity at the

Table 12. Physical properties of additional soils used in soil CLC analysis of ^{99}Tc.[1]

Soil Series	Subgroup Classification	Horizon	Location (Minn. Co.)	Depth Sampled (in)	Particle Size (% dry weight)			Surface Area (m^2/g)	Water Retention (g_{H_2O}/g dry soil)	
					Sand	Silt	Clay		1/3 bar	15 bar
Bearden	Aeric Calciaquolls	Ap	Norman	0-6	7.3	62.0	30.7	187	0.37	0.24
		Clca, C2ca		18-24	12.6	63.8	23.6	96	0.27	0.14
Blue Earth	Cumulic Haplaquolls	Ap	Watonwan	0-6	9.3	56.2	34.5	186	0.63	0.40
		Bg		18-24	15.7	52.7	31.6	178	0.59	0.38
Brainerd	Aquic Fragiochrepts	A1, A2	Crow Wing	0-6	52.9	34.7	12.4	87	0.24	0.15
		A&B, B&A		21-27	74.1	19.6	6.3	94	0.09	0.05
Canisteo	Typic Haplaquolls	A1	Steele	0-5	37.3	32.3	30.4	160	0.37	0.29
		Bg		17-23	46.4	28.7	24.9	270	0.25	0.15
Fargo	Vertic Haplaquolls	Ap	Norman	0-6	1.2	48.9	49.9	324	0.43	0.32
		B1g		14-18	1.0	44.7	54.3	382	0.39	0.28
Fayette	Typic Hapludalfs	A1, A2	Olmsted	0-6	6.8	76.2	17.0	85	0.29	0.13
		B2t		16-22	6.6	66.5	26.9	155	0.28	0.14
Hegne	Typic Calciaquolls	Ap	Norman	0-6	4.4	49.3	46.3	343	0.43	0.31
		C2ca		14-18	1.5	49.1	49.4	269	0.31	0.22
Hubbard	Udic Haploborolls	Ap	Sherburne	0-6	83.1	10.1	6.8	60	0.09	0.04
		B2		16-20	83.9	10.4	5.7	52	0.08	0.04
Kranzburg	Udic Haploborolls	Ap	Pipestone	0-6	7.5	60.4	32.1	224	0.18	0.16
		B21		15-21	5.4	62.6	32.0	227	0.18	0.16
Lester	Mollic Hapludalfs	A1, A2	Steele	0-6	61.2	25.1	13.7	100	0.18	0.09
		B2t		16-22	58.5	21.6	19.9	172	0.19	0.08
Milaca	Typic Fragiochrepts	A1, A2	Benton	0-6	62.0	21.2	6.8	24	0.17	0.06
		B21x		20-26	68.1	25.7	6.2	73	0.11	0.04
Nicollet	Aquic Hapludolls	Ap	Steele	0-6	40.1	38.0	21.9	150	0.24	0.12
		B2		15-21	45.9	30.1	24.0	166	0.23	0.11
Ontonagon	Typic Eutroboralfs	A2	Carlton	1-6	8.8	31.8	59.4	209	0.36	0.22
		B2t		10-16	1.7	7.3	91.0	341	0.47	0.27
Ulen	Aquic Haploborolls	Ap	Norman	0-6	77.3	10.3	12.4	101	0.15	0.08
		Clca		19-25	85.7	7.8	6.5	48	0.07	0.03
Zimmerman	Alfic Udipsamments	A1, A3	Sherburne	0-6	93.7	3.0	3.1	19	0.06	0.03
		B or C1		15-21	95.1	2.6	2.3	52	0.03	0.02
Svea	Pachic Udic Haploborolls	B21, B22	Swift	14-21	22.5	52.1	25.4	162	0.32	0.21

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[1] Characterized by Pluth et al. (1970).

Table 13. Chemical properties of additional soils used in soil CLC analysis of ^{99}Tc[1].

Soil Series		pH_{H_2O}	Organic Carbon	$CaCO_3$ Equivalent	Free Iron Oxide	CEC	Extractable P	Exchangeable K
			---------(%)---------		(%)	(meq/100g)	(lbs/acre)	(ppm)
Bearden	A[2]	7.7	3.00	---	0.2	30.6	1.6	230
	B[3]	8.0	0.10	---	0.2	9.4	0.8	80
Blue Earth	A	7.7	11.0	2.2	0.5	36.4	1.6	215
	B	7.6	8.3	2.4	0.4	27.0	1.6	125
Brainerd	A	5.4	3.0	---	1.1	15.2	16.0	100
	B	5.4	0.10	---	1.3	5.8	2.0	30
Canisteo	A	7.8	7.30	1.0	0.3	43.5	1.6	170
	B	7.9	0.60	1.1	0.2	18.8	1.2	135
Fargo	A	7.0	5.20	---	0.7	45.2	1.2	780
	B	7.2	1.70	0.2	0.9	38.4	0	350
Fayette	A	5.4	2.30	---	1.0	15.1	30.8	165
	B	5.5	0.50	---	1.4	37.8	6.0	120
Hegne	A	8.0	4.30	1.7	0.2	37.8	2.2	300
	B	7.8	0.60	3.3	0.3	35.6	3.0	280
Hubbard	A	5.8	1.00	---	0.6	6.4	8.8	65
	B	6.0	0.40	---	0.7	4.9	3.2	20
Kranzburg	A	6.6	3.10	---	1.2	26.8	2.4	135
	B	7.3	1.00	---	1.2	23.8	1.6	130
Lester	A	6.3	2.30	---	0.8	16.4	6.0	100
	B	5.5	0.40	---	1.1	9.0	2.4	85
Milaca	A	5.7	1.70	---	1.5	6.2	22.0	60
	B	5.6	0.20	---	1.6	22.0	3.2	45
Nicollet	A	6.0	2.80	---	0.7	20.4	10.4	95
	B	5.3	0.60	---	0.8	15.4	2.0	95
Ontonagon	A	5.2	3.50	---	2.9	40.2	6.4	200
	B	6.5	0.60	---	2.3	44.4	4.8	265
Ulen	A	8.3	1.80	1.2	0.2	11.7	8.0	60
	B	8.6	0.30	2.7	0.3	2.2	4.0	25
Zimmerman	A	5.5	0.7	---	0.5	3.8	10.8	40
	B	5.7	0.2	---	0.6	3.2	12.8	20
Svea	B	6.4	0.8	---	1.2	18.7	0.8	135

[1] Characterized by Pluth et al. (1970).

[2] Surface

[3] Subsurface

Table 14. Chromatographic distribution of ^{99}Tc in 41 Minnesota soils.

Soil Series		R_f	R_f class[1]	R_p	R_b	K_d	D_b (g/cm^3)	Porosity (cm^3/cm^3)
Waukegan		0.98	5	0.76	0.49	7.27×10^{-3}	1.40	0.43
Bearden		0.81[4]	4[3]	0.69	0.23	1.18×10^{-1}	1.17	0.53
Hegne		1.00	5	0.93	0.33	0.00	1.28	0.45
Bergland		0.94	5	0.80	0.28	2.47×10^{-2}	1.16	0.44
Omega		0.97	5	0.78	0.10	6.62×10^{-3}	1.66	0.37
Zimmerman		0.96	5	0.90	0.67	9.93×10^{-3}	1.57	0.40
Nicollet Surface		0.96	5	0.79	0.50	1.14×10^{-2}	1.59	0.39
Nicollet Subsurf.		1.00	5	0.89	0.46	0.00	1.49	0.43
Hibbing		0.78[4]	4[3]	0.71	0.44	6.76×10^{-2}	1.62	0.38
Arveson		0.87	4	0.77	0.60	5.37×10^{-2}	1.28	0.48
Bearden[2]	A	1.00	5	0.59	.24	0.00	1.32	0.48
	B	1.00	5	0.84	.42	0.00	1.56	0.41
Blue Earth[2]	A	0.84[4]	4	0.84	.42	1.18×10^{-1}	0.92	0.58
	B	0.75[4]	4	0.75	.35	2.83×10^{-1}	0.75	0.65
Brainerd[2]	A	0.68[4]	4[3]	0.58	.29	1.55×10^{-1}	1.39	0.45
	B	0.98	5	0.88	.39	2.86×10^{-3}	1.93	0.28
Canisteo[2]	A	0.84[4]	4[3]	0.42	.11	7.57×10^{-2}	1.21	0.50
	B	1.00	5	0.95	.32	0.00	1.42	0.47
Fargo[2]	A	0.92	5	0.82	.31	2.12×10^{-2}	1.48	0.38
	B	1.00	5	0.82	.23	0.00	1.92	0.23
Fayette[2]	A	0.95	5	0.86	.45	1.85×10^{-2}	1.31	0.48
	B	0.95	5	0.89	.37	2.45×10^{-2}	1.15	0.56
Hegne[2]	A	1.00	5	0.93	.31	0.00	1.51	0.39
	B	1.00	5	0.94	.24	0.00	1.39	0.46
Hubbard[2]	A	0.85	4	0.77	.51	5.84×10^{-2}	1.38	0.47
	B	1.00	5	0.97	.62	0.00	1.84	0.31
Kranzburg[2]	A	1.00	5[3]	0.76	.38	0.00	0.89	0.64
	B	1.00	5	1.00	.59	0.00	0.87	0.67
Lester[2]	A	0.90	5	0.78	.45	3.78×10^{-2}	1.39	0.45
	B	1.00	5	1.00	.47	0.00	1.52	0.41
Milaca[2]	A	0.86	4	0.79	.59	5.17×10^{-2}	1.44	0.44
	B	1.00	5	0.90	.68	0.00	1.67	0.36
Nicollet[2]	A	0.84[4]	4	0.73	.21	7.79×10^{-2}	1.26	0.50
	B	1.00	5	0.91	.30	0.00	1.53	0.40
Ontonagon[2]	A	0.97	5	0.97	.19	6.97×10^{-3}	1.51	0.39
	B	0.93	5	0.74	0	2.98×10^{-2}	1.30	0.48
Ulen[2]	A	1.00	5[3]	0.93	.70	0.00	1.82	0.31
	B	1.00	5	0.93	.75	0.00	1.53	0.44
Zimmerman[2]	A	0.92[4]	5	0.92	.50	2.18×10^{-2}	1.62	0.39
	B	0.80	4	0.80	.43	5.07×10^{-2}	1.73	0.34
Svea[2]	B	1.00	5	0.92	.51	0.00	1.49	0.40

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[1] Helling and Turner, 1968.

[2] Characterized by Pluth et al. (1970).

[3] Soils used for subsequent study of Cl^- and movement of ^{99}Tc in soil columns.

[4] R_f significantly less than unity.

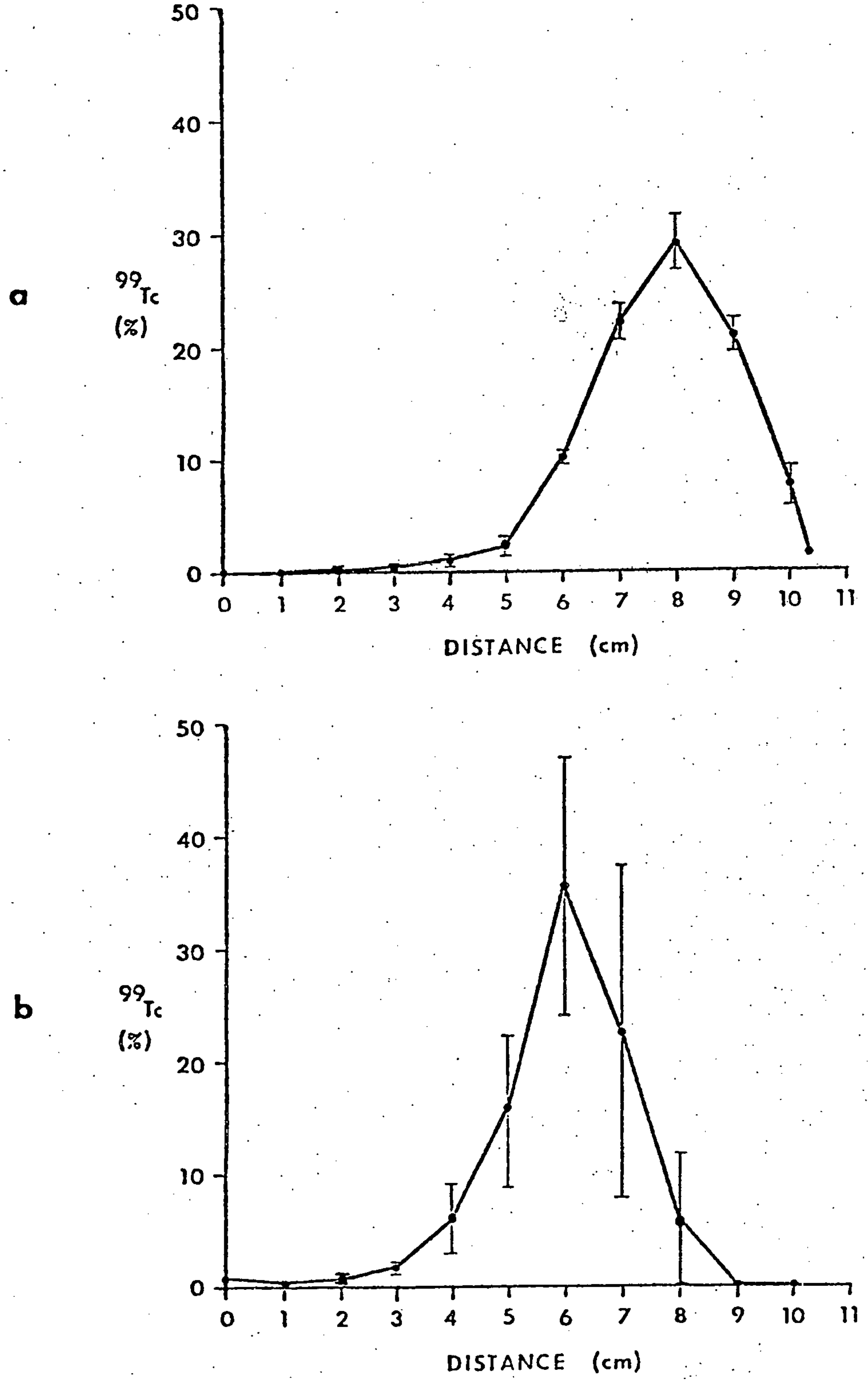


Figure 20. Soil CLC elution distribution of ^{99}Tc for Nicollet surface (a) and Hibbing surface (b). Values represent means of triplicate samples with standard errors indicated by brackets.

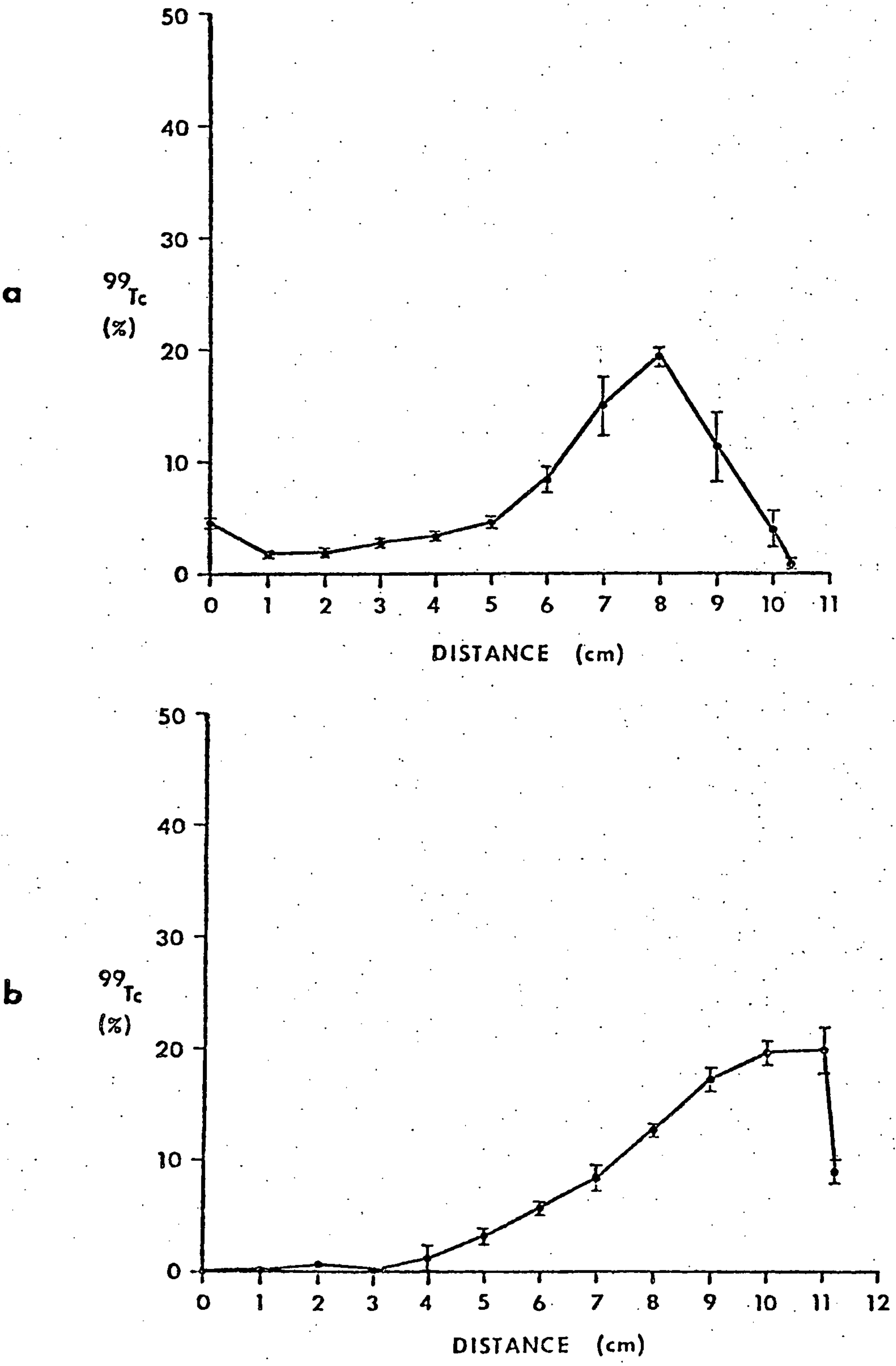


Figure 21. Soil CLC elution distribution of ^{99}Tc for Omega surface (a) and Hegne surface (b). Values represent means of triplicate samples with standard errors indicated by brackets.

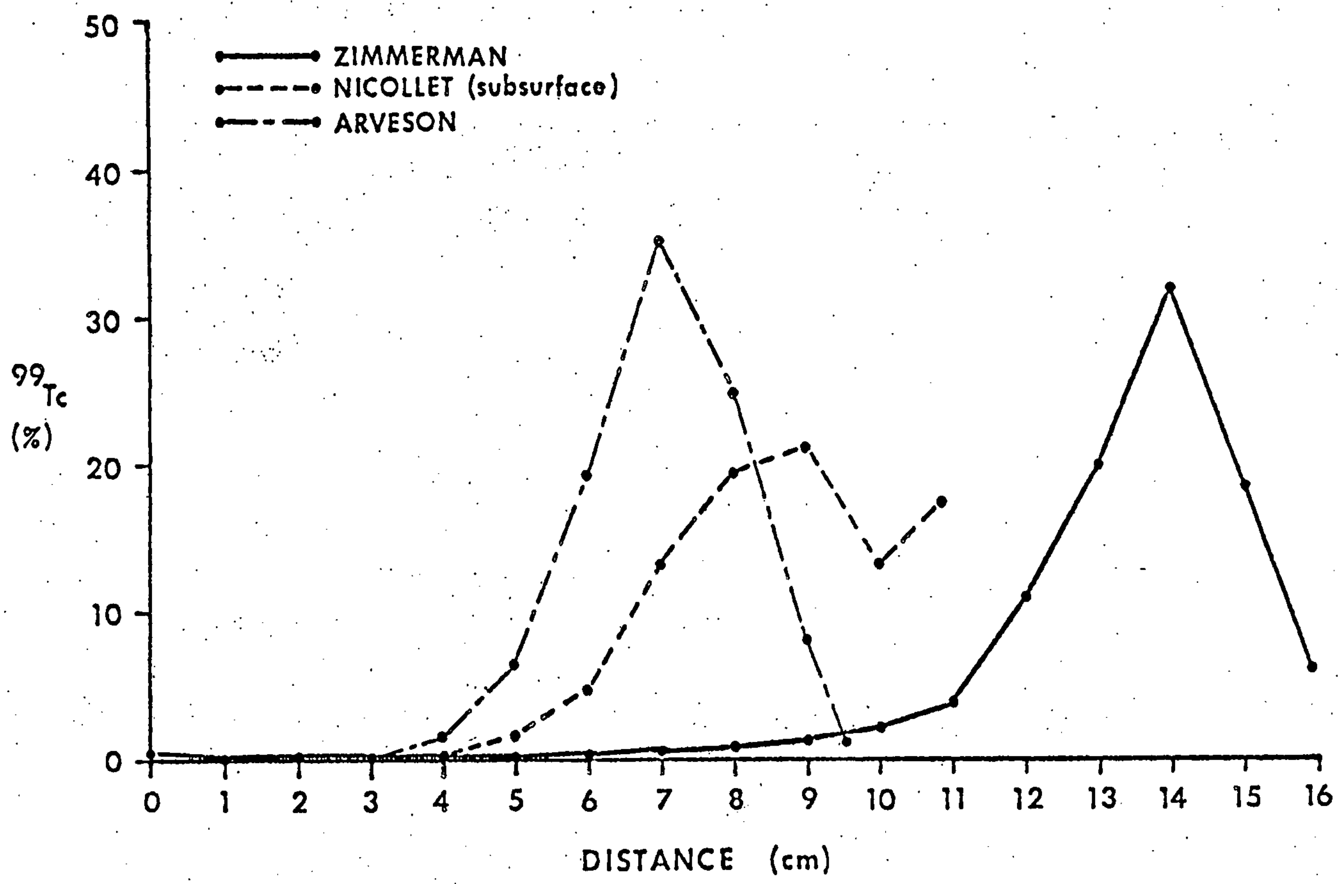


Figure 22. Soil CLC elution distribution of ^{99}Tc for Zimmerman surface, Nicollet subsurface, and Arveson surface. Values represent means of triplicate samples.

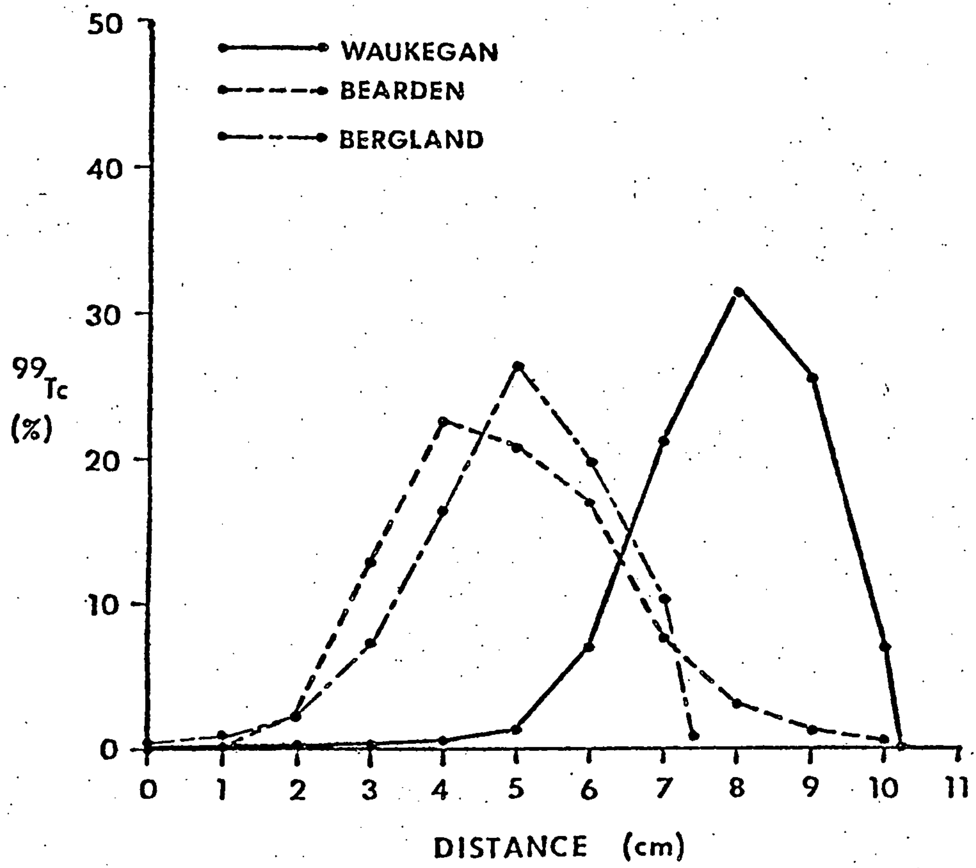


Figure 23. Soil CLC elution distribution of ^{99}Tc for Waukegan surface, Bearden surface, and Bergland surface. Values represent means of triplicate samples.

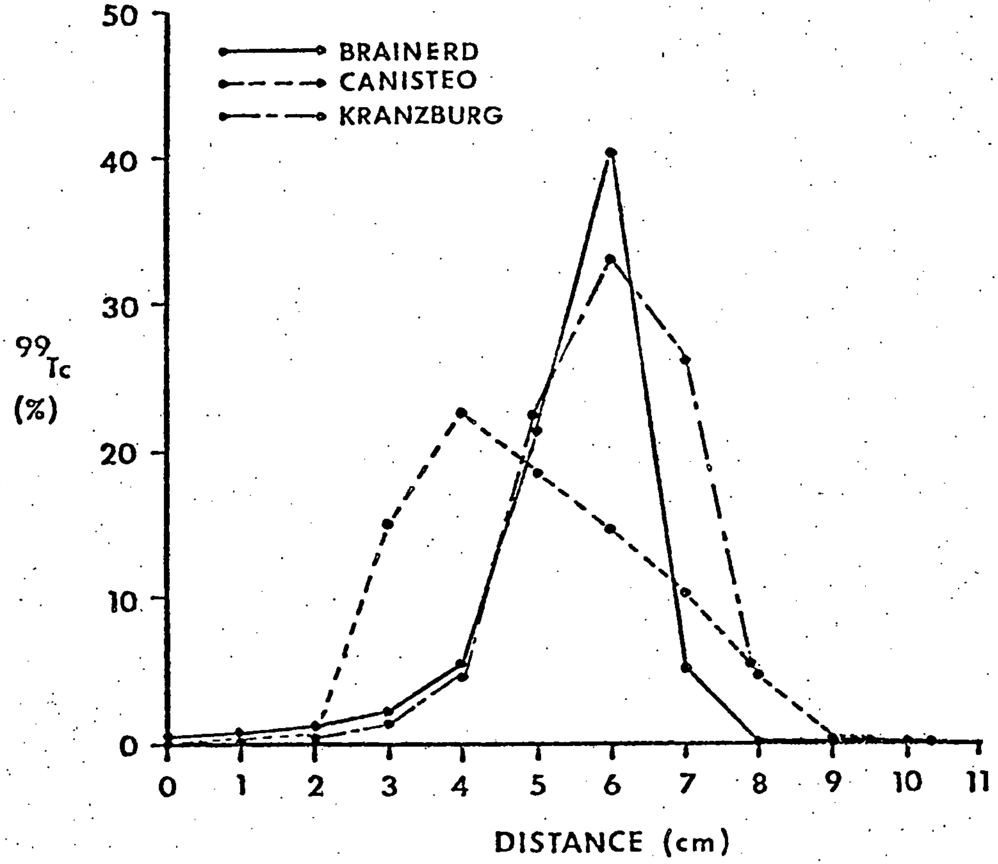


Figure 24. Soil CLC elution distribution of ^{99}Tc for Brainerd surface, Canisteo surface, and Kranzburg surface. Values represent means of triplicate samples.

0.05 level (Snedecor and Cochran, 1967). R_f values of unity imply that at least some of the radionuclide moved with the water front. Those soils with R_f values less than unity included Bearden, Hibbing, Brainerd surface, Blue Earth surface, Blue Earth subsurface, Zimmerman subsurface, Canisteo surface, and Nicollet surface. These soils all have class 4 R_f (Helling and Turner, 1968). In order to gain a more complete concept of ^{99}Tc movement, all the 'R' factors must be considered as a distribution pattern. These parameters will be discussed with consideration of current chromatographic and miscible displacement theories.

The bulk movement of water in soil as described by Darcy's Law has proven inadequate for clear definition of the movement and distribution of solutes in the soil system (Nielson and Bigger, 1961). The movement of ionic and molecular species in the soil water system is governed by mass flow (convection), diffusion, hydrodynamic dispersion, and chemical adsorption. The complex dynamics of solute and solvent flow with soil surface interaction has been characterized in terms of chromatographic and miscible displacement models (Bigger and Nielson, 1963; Breener et al., 1965; Frissel and Poelstra, 1967; Kirkham and Powers, 1972; Nielson and Bigger, 1961).

Distribution of ^{36}Cl in soil CLC: The six soils chromatographically eluted with $^{36}Cl^-$ were selected to represent the range of R_f values for ^{99}Tc found in the soil CLC analysis. The distinct Poisson distribution of $^{36}Cl^-$ for the Canisteo, Nicollet, Ulen, Brainerd and Kranzburg surface soils with R_f of unity suggests that there is little inorganic anion exchange occurring (Table 15 and Figures 25-26). The $^{36}Cl^-$ distribution in the Hibbing soil presents an anomalous situation with obvious retention of chloride in the column (Figure 26). In this case retention could have

Table 15. Chromatographic distribution pattern of ^{36}Cl.

Soil Series	R_f	R_f class	R_p	R_b	K_d	D_b (g/cm^3)	Porosity (cm^3/cm^3)
Nicollet surface	1.00	5	1.00	.51	0.00	1.55	0.41
Hibbing	.85	4	.09	0	4.60×10^{-2}	1.56	0.40
Ulen[1]	1.00	5	1.00	.19	0.00	1.69	0.36
Brainerd[1]	1.00	5	1.00	.67	0.00	1.45	0.43
Canisteo[1]	1.00	5	1.00	.80	0.00	1.21	0.50
Kranzburg[1]	1.00	5	1.00	.61	0.00	1.32	0.47

[1] Soils characterized by Pluth et al. (1970).

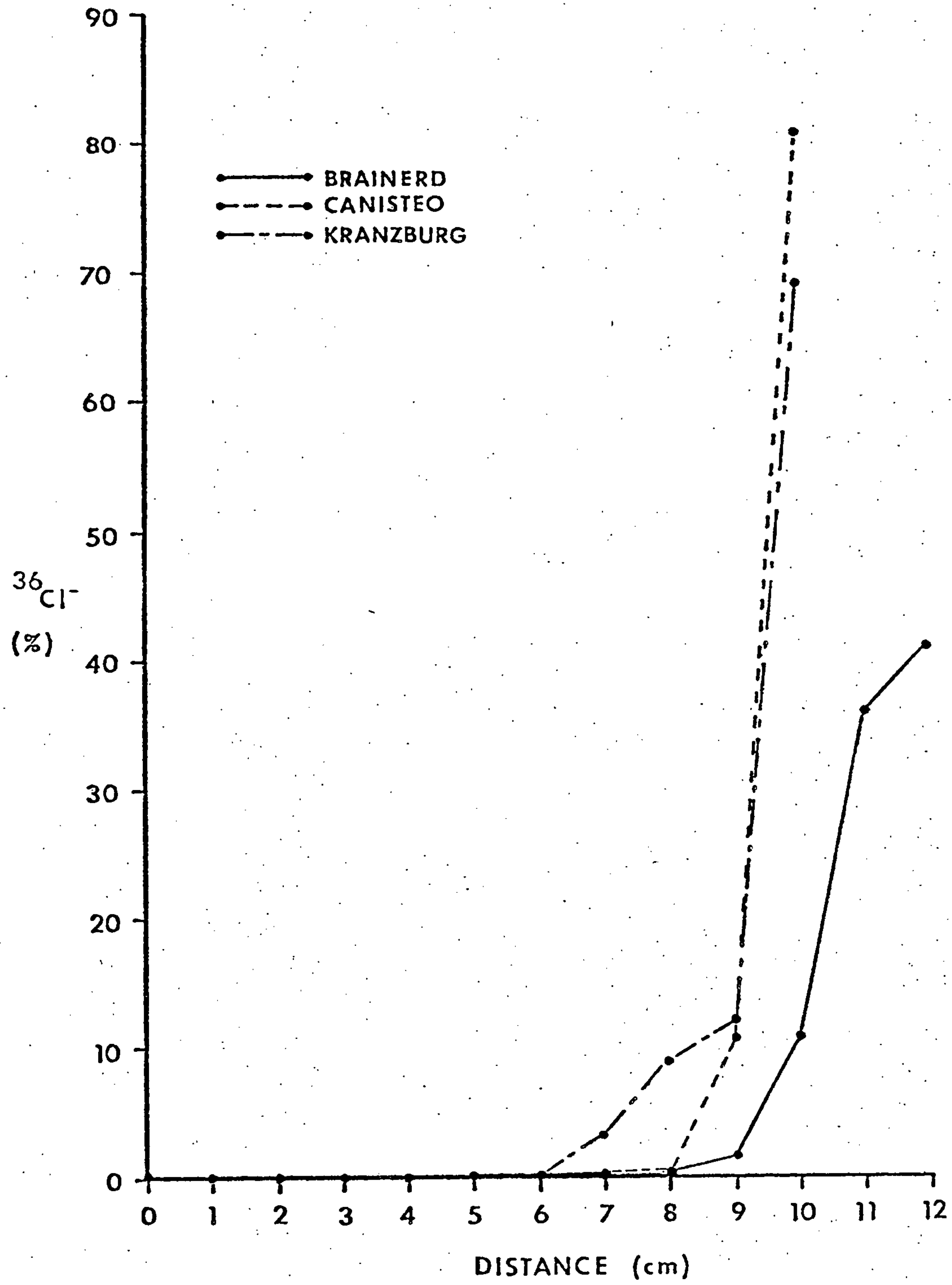


Figure 25. Soil CLC elution distribution of $^{36}Cl^-$ for Brainerd surface, Canisteo surface, and Kranzburg surface. Values represent means of triplicate samples.

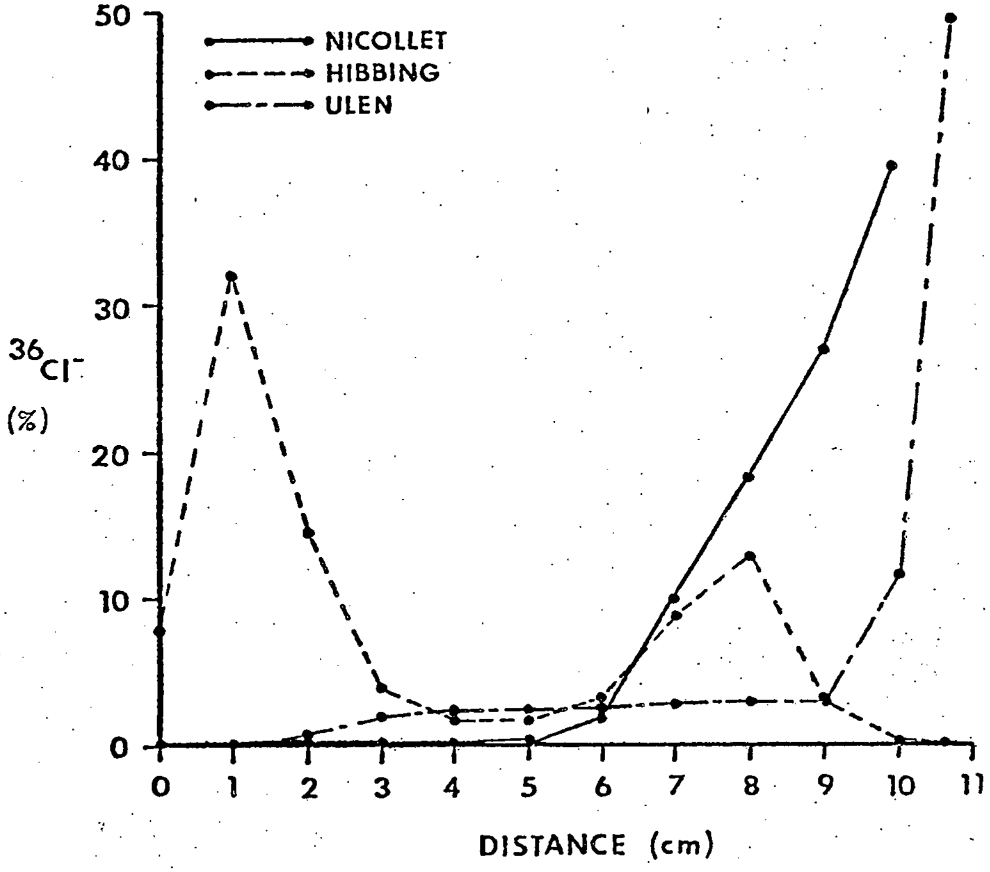


Figure 26. Soil CLC elution distribution of $^{36}Cl^-$ for Nicollet surface, Hibbing surface, and Ulen surface. Values represent means of triplicate samples.

been prompted by a combination of low pH and relatively high iron oxide content creating an anion exchange potential higher than for the other five soils (Mott, 1970). A high silt content in the Hibbing soil with many CLC column micropores would increase solute retention in these stagnant sinks. However, because Minnesota soils are generally dominated by three-layer clays and low hydrous oxide content, retention of $^{36}Cl^-$ by inorganic anion exchange appears to be unlikely in most cases.

Comparing the $^{36}Cl^-$ distribution patterns, as a standard for a non-sorbing anion, to the ^{99}Tc distributions, shows a definitely increased retention of ^{99}Tc in terms of tailing and R factor retardation (Figures 20, 23, 24, 25, 26 and Tables 14 and 15). It is obvious that some retention mechanism is responsible for the decreased ^{99}Tc flux in comparison to $^{36}Cl^-$. This increased retardation of ^{99}Tc is in addition to unsaturated miscible displacement, as demonstrated by the asymmetric nature of the distribution curves.

Although inorganic anion exchange retention may be partially responsible for ^{99}Tc retention in the Hibbing soil, the general trend for the soils analyzed does not indicate this mechanism will operate in most cases. Soils used in this study were also fairly low in hydrous oxides (Berg and Thomas, 1959; Pluth et al., 1970). This does not suggest that the anion exchange capacity that does exist in these soils will not affect the ^{99}Tc distribution.

In basic anion exchange resins TcO_4^- is more selectively absorbed than is Cl^- (Markl and Bobleter, 1966; Ryabchikov and Pozdnyakov, 1965). The pertechnate ion is often removed from these anion exchange resins with nitrate and perchlorate ions. This selective sorption may be a result of the pertechnate ion having a smaller hydration sphere than the chloride ion (Kawashima, 1962; Kotegov et al., 1968; Markl and Bobleter, 1966;

Ryabchikov and Pozdnyakov, 1965). These trends could indicate that ^{99}Tc is held with greater tenacity by the weak soil anion exchange complex than is $^{36}Cl^-$, but with less vigor than the nitrate ion. This could partially account for the greater mobility of the chloride ion in comparison to the pertechnate ion, at least under acidic conditions in the soil CLC.

The maximum elution time of any of the soil CLC plates did not exceed twenty-five hours. Within this time, no fixed sorption of ^{99}Tc has been found in this study or by Wildung et al. (1974). The hypothetical microbial fixation or organic matter interaction as found in the static sorption experiments is not operating strongly in these short times.

Considering the stability of the pertechnate ion in the range of the given soils pH's and oxidation potentials under the aerobic soil CLC conditions, it is unlikely that ^{99}Tc (VII) will be reduced and precipitated as insoluble oxides or sulfides (Kotegov et al., 1968).

All of the soils chromatographically studied were divided into two groups for statistical analysis based upon difference of mean soil parameters. We separated those soils with R_f values not significantly different from unity from those soils with R_f values significantly less than unity. The mean soil parameters were determined for both groups and compared via the t-test (Snedecor and Cochran, 1967). At the 0.05 level the only parameter significantly different was organic matter content. Another group separation was based upon R_f classes, with one group as class 5 (R_f = 1.00-0.90) and the other as class 4 (R_f = 0.89-0.65) (Helling and Turner, 1968). Again the t-test showed the organic matter content to be the only significantly different soil parameter. Statistically, higher organic matter in selected Minnesota soils is related to retardation of frontal ^{99}Tc movement.

It is particularly worth noting that there were no significant differences in free iron oxide content, pH, percent clay, or surface area among soils in the two R_f groups. On a statistical basis this indicates that inorganic anion exchange capacity of a soil does not hinder frontal transport of ^{99}Tc in the studied soils. This does not mean that anion exchange does not function in asymmetrical tailing of ^{99}Tc distributions.

Regression analysis of the R_f and K_d parameters with soil parameters did not indicate any significant relationships. This may have occurred because the R_f and K_d values of many soils were not significantly different.

Visual inspection of the soil parameters in class 4 indicates that there is comparatively high organic matter in the Bearden, Blue Earth surface and subsurface, Brainerd surface, and Canisteo surface soils. However in the Hibbing, Arveson, Hubbard surface, Nicollet surface, and Zimmerman subsurface soils the organic matter content is not dissimilar to that in many class 5 soils. The lower R_f in these cases may be due to greater unsaturated dispersion and diffusion related to clay and silt micropores with secondary weak retention by organic matter. Possibly the structural composition of the organic matter could also be related to ^{99}Tc elution retention.

As previously mentioned, ^{99}Tc solvent extraction and separation on anion exchange resin is facilitated by the presence of basic electron donor groups. Increased O:C atom ratio of the extracting organic solvent with increased polar concentration will increase the extraction of the pertechnate ion (Boyd and Larson, 1960). Aromatic substituted compounds, ketones, alcohols, amines, and organo-phosphorous compounds also extract the relatively unhydrated ^{99}Tc (VII) quite readily (Richards and Steigman, 1974). In general, organic molecules with highly polar basic functional groups will promote the retention of the pertechnate ions. This suggests that the polar fulvic and humic acid fraction of the soil organic matter could be potentially responsible for additional ^{99}Tc column retention and asymmetric distribution patterns.

Including the class 5 soils in this qualitative analysis, the polar organic matter substrate could be contributing to the ^{99}Tc soil CLC tailing, particularly for the soils with a lower pH. Tailing also increased for those soils with relatively high silt and clay content, although the R_f value may have been in the range of unity. The greater number of stagnant micropore sinks for finer textured soils would provide a greater diffusion retention of ^{99}Tc. However, the relatively slow water front movement in these soils, particularly for the clays, would allow greater diffusion and dispersion of the pertechnate ion with the water front. This would cause an R_f value approaching unity, but also allow for increased column tailing compounded by the presence of the organic matter.

In sandy soils the degree of tailing is not as great, as micropore diffusion sinks for ^{99}Tc are not as numerous. This situation will be modified by the amount of organic matter present in the soil. Unsaturated dispersion and diffusion effects appear to be operating to such an extent, however, that the Zimmerman subsurface soil did significantly retain ^{99}Tc in the thin layer column. Of course, it should be realized these postulated retention forces are not very tenacious. This is exemplified by the ease and nearly complete extraction of the pertechnate ion with the $CaCl_2$ solution from the soil CLC segments. The concentrated ^{99}Tc in the column 'spot' is initially held by the soil organic matter as well as by other anion exchange mechanisms. As the solution is displaced upward in the thin-layer column the organic matter is no longer able to hold the pertechnate ion against the decreasing concentration gradient. These factors, including miscible displacement behavior in the soil CLC columns, will create the various asymmetric elution distributions observed for the movement of ^{99}Tc (Figures 20-24 and Table 14-15).

The soils characterized for soil CLC in this report and by Pluth et al., (1970) had duplicate soil series samples including Nicollet surface and subsurface, Hegne surface, and Zimmerman surface. The elution patterns for the Nicollet subsurface, Hegne surface, and Zimmerman surface were similar. However, for the Bearden surface and Nicollet surface there was a R_f class difference between samples from the same series. Although the frontal movement was differentially retained the distribution pattern itself was similar. This observed difference in behavior demonstrates that variability can be expected within samples from the same soil series, as well as between series.

<u>Conventional Soil Column Elution of ^{99}Tc</u>: The six representative soils used for ^{36}Cl$^-$ soil CLC were also used for the conventional column elution of ^{99}Tc. The conditions of each soil column (Table 16) and the ^{99}Tc elution patterns (Figures 27-32) were monitored for these six soils. For all columns the ^{99}Tc leaching behavior exhibited the asymmetric pattern of anion flow as described by the miscible displacement studies previously cited. In all cases some measurable ^{99}Tc was present in the first milliliter aliquot of the leaching solution. The major portion of the ^{99}Tc was eluted in the next four aliquots. Only the Brainerd surface soil exhibited any appreciable tailing. The slight tailing in most cases indicates that ^{99}Tc retention forces are not very effective under these leaching conditions.

The major concentration of the pertechnate ion appearing in the first few aliquots was probably a result of the ^{99}Tc solution moving through the very large pores quite rapidly (Peterson and Dixon, 1971). During the column elution the bulk of the added aliquot could be observed passing

Table 16. Soil column leaching parameters used to monitor movement of ^{99}Tc.

Soil Series	Bulk Density (g/cm^3)	Porosity (cm^3/cm^3)	Suction (bars)	Aliquot Drainage Time (minutes)	Depth of Column (cm)
Nicollet Surface	1.07	0.59	0.33	10	5
Hibbing Surface	1.18	0.55	0.33	60	5
Ulen Surface	1.22	0.54	0.10	10	5
Brainerd Surface	1.04	0.59	0.33	15	5
Canisteo Surface	0.96	0.60	0.10	10	5
Kranzburg Surface	1.04	0.58	0.33	30	5

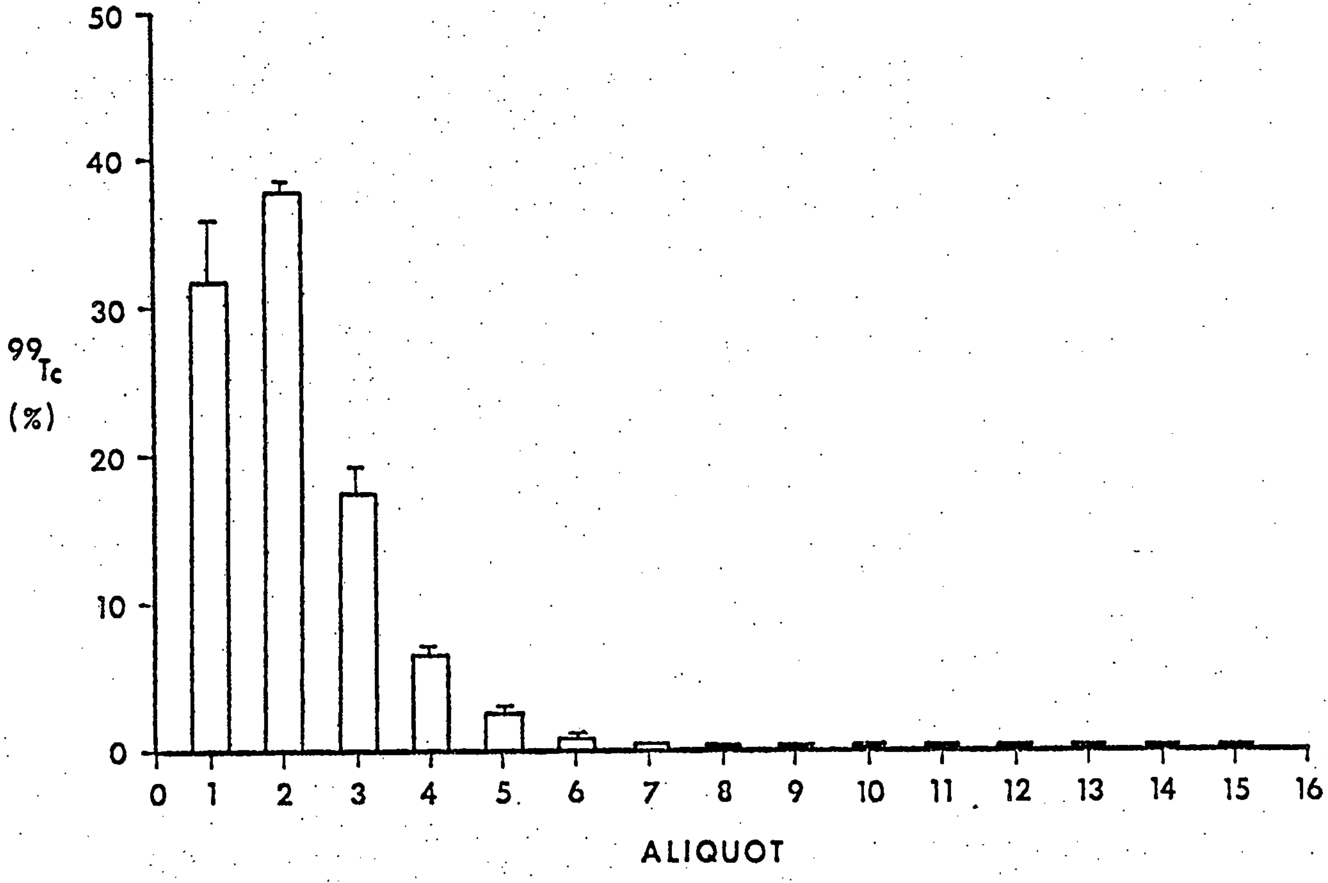


Figure 27. Conventional soil column leaching distribution of ^{99}Tc for Nicollet surface. Values represent means of triplicate samples with standard errors indicated by the bracket at the top of each bar.

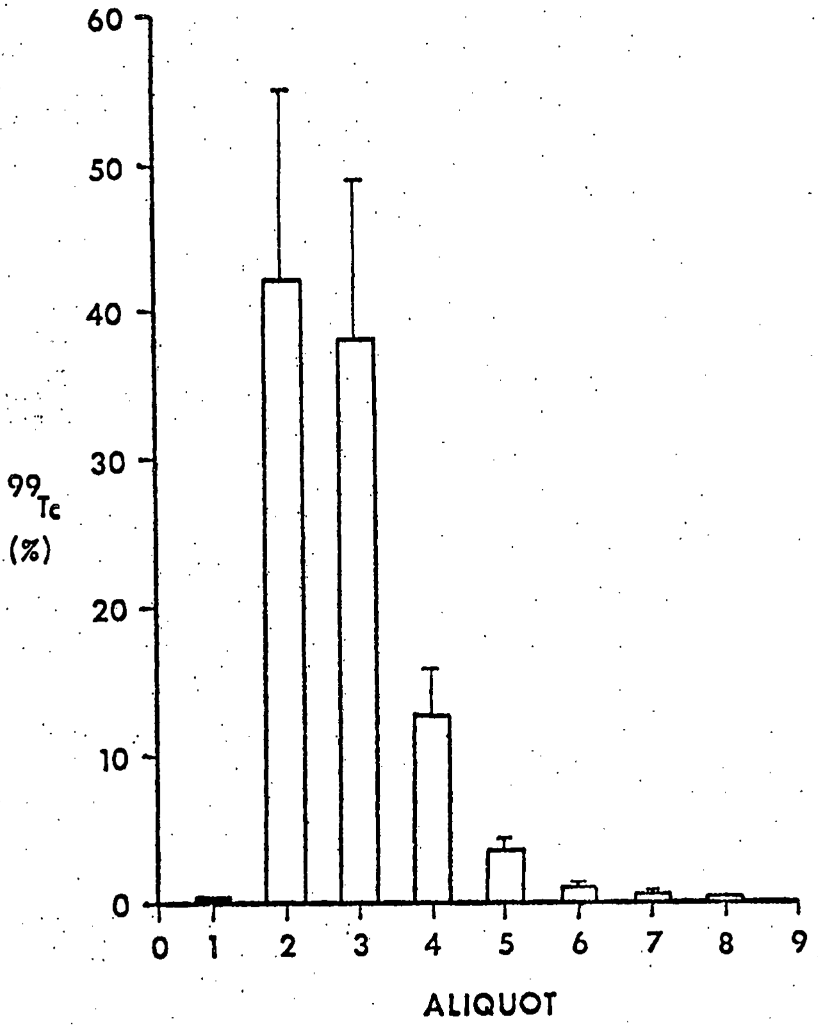
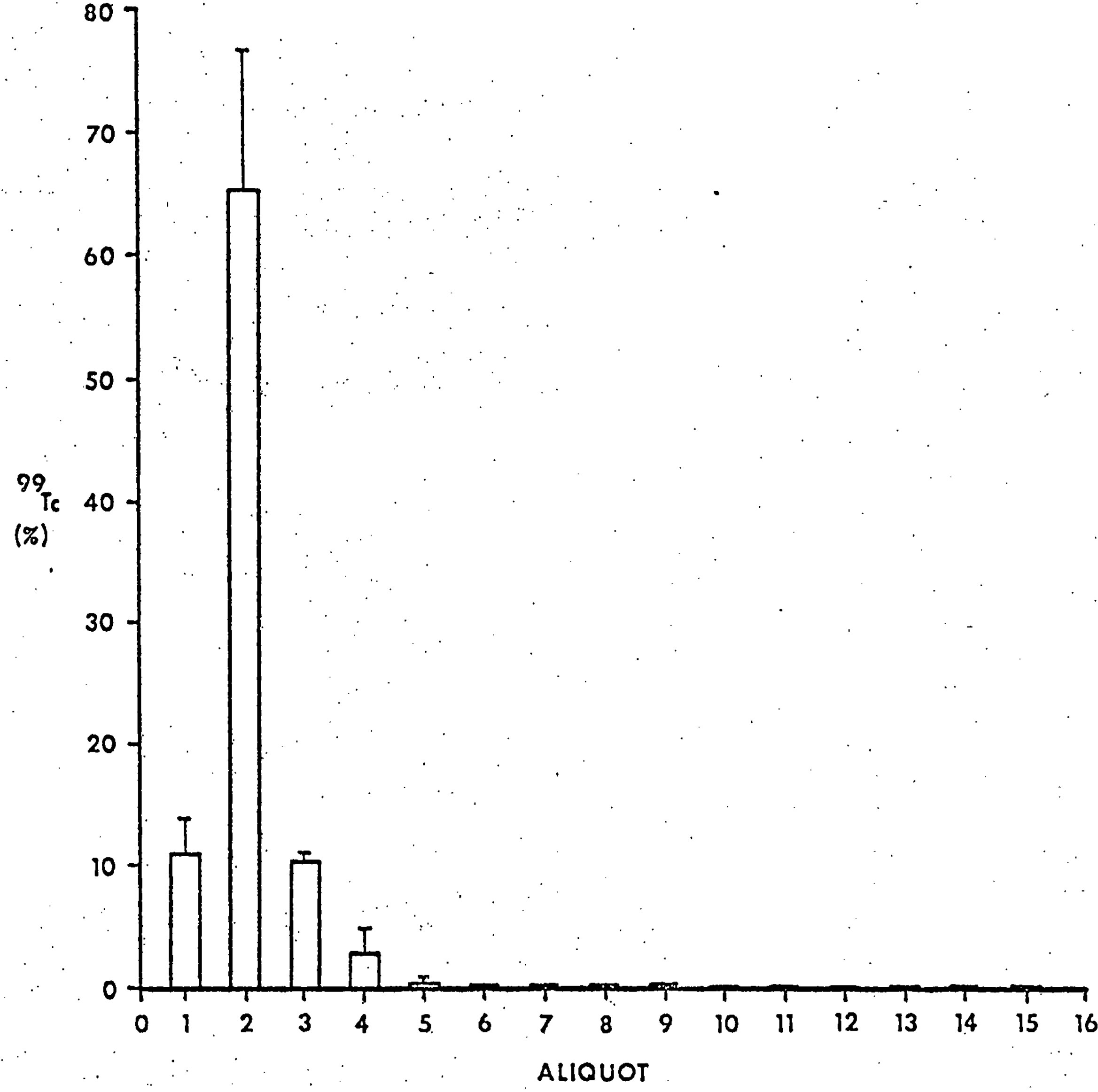


Figure 28. Conventional soil column leaching distribution of ^{99}Tc for Hibbing surface. Values represent means of triplicate samples with standard errors indicated by the bracket at the top of each bar.

Figure 29. Conventional soil column leaching distribution of ^{99}Tc for Ulen surface. Values represent means of triplicate samples with standard errors indicated by the bracket at the top of each bar.



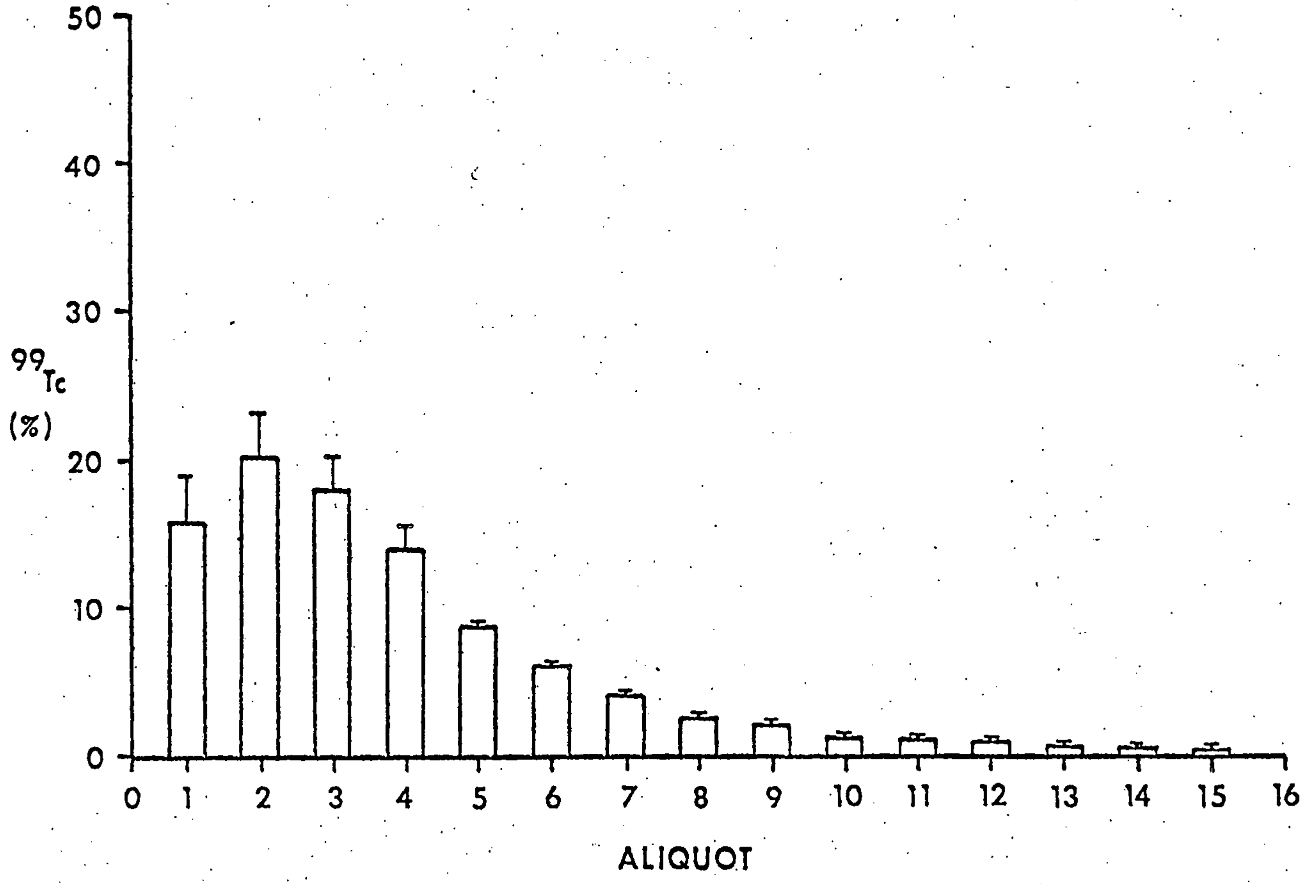


Figure 30. Conventional soil column leaching distribution of ^{99}Tc for Brainerd surface. Values represent means of triplicate samples with standard errors indicated by the brackets at the top of each bar.

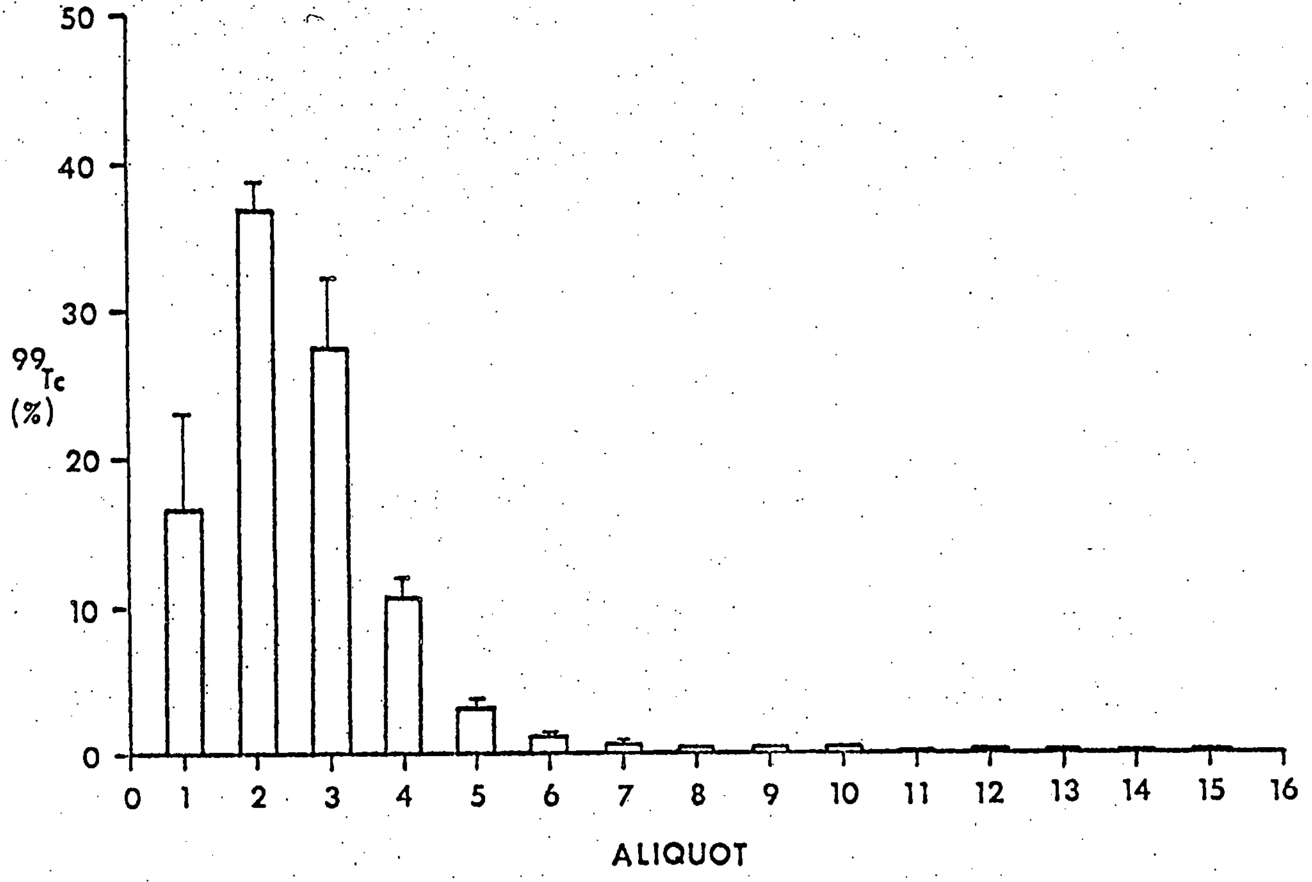
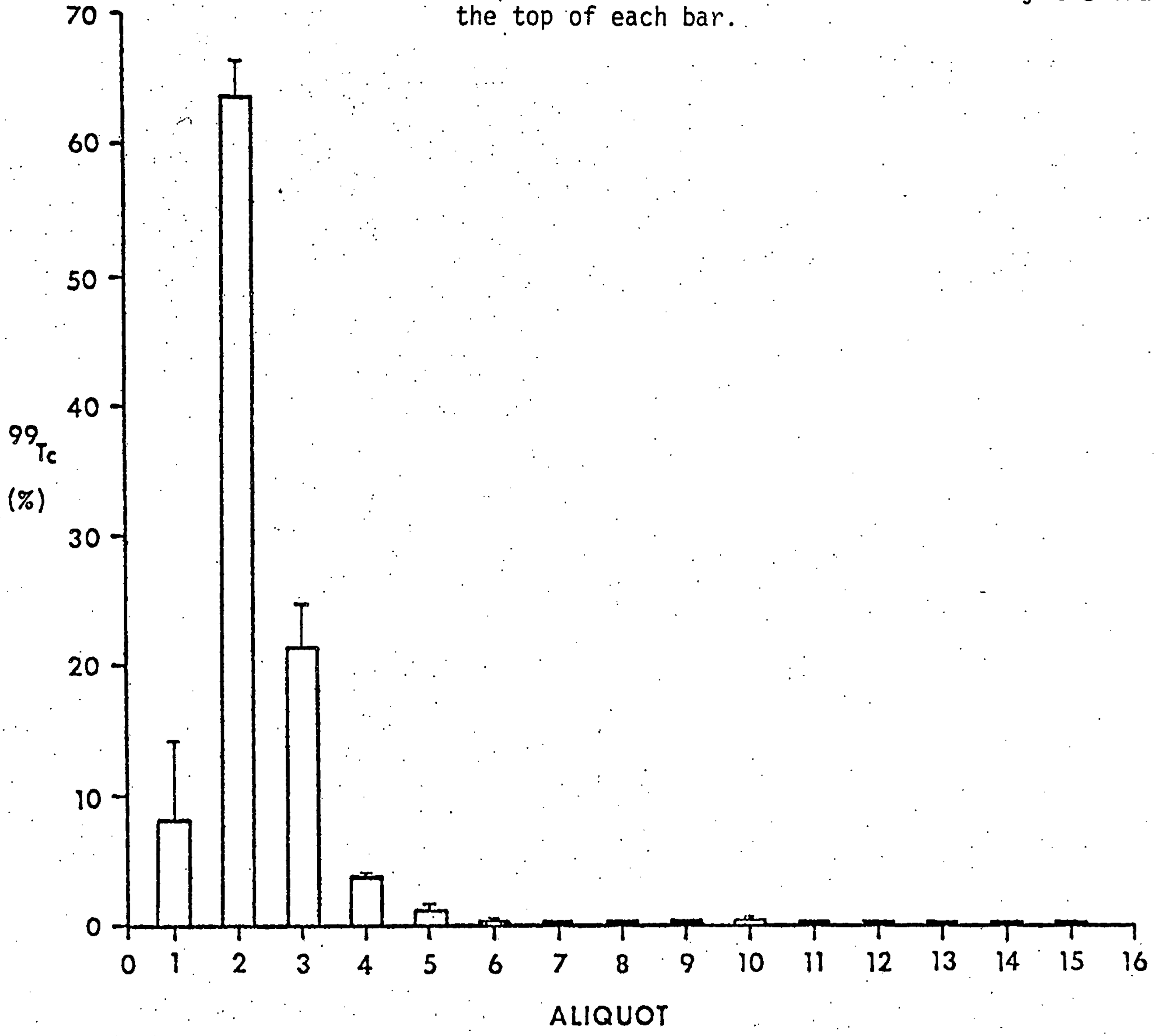


Figure 31. Conventional soil column leaching distribution of ^{99}Tc for Canisteo surface. Values represent means of triplicate samples with standard errors indicated by the brackets at the top of each bar.

Figure 32. Conventional soil column leaching distribution of ^{99}Tc for Kranzburg surface. Values represent means of triplicate samples with standard errors indicated by the brackets at the top of each bar.



through the large inter-aggregate pores. The residual ^{99}Tc was retained in the aggregate micropore solution sinks. Possibly with greater column depth and under continuous flow, greater elution curve resolution may have been achieved. However, under the present conditions, the ^{99}Tc flow in these conventional soil columns appears to be similar to non-sorbing anion flow. The rapid rate of elution may have prevented an equilibrium to occur between the soil organic matter polar substrate and the pertechnate ion.

General Comments on the Movement of ^{99}Tc through Minnesota Soils: With the soil CLC modeling solute movement in aggregates and conventional columns approximating macropore and channel flow a general trend in pertechnate flow in selected Minnesota soils has been observed. ^{99}Tc moves through the soil as a relatively large anion exhibiting characteristic miscible displacement with some asymmetric tailing. ^{99}Tc exhibits greater retention than Cl^-, which may be attributed statistically to weak binding by organic matter. Anion exchange processes induced by clay and oxide surfaces appear to be very weak as chemical retention factors. It is questionable whether this retention phenomenon is related to the static sorption activity reported in the first part of this study. The soil CLC and conventional columns are short term, dynamic, aerobic systems. The sorption observed previously was related to long term, static, and usually anaerobic conditions. Generally under the present experimental parameters ^{99}Tc remains quite mobile in the studied Minnesota soils.

Translating these results to a more general situation, it might be expected in a field situation that at least some of any ^{99}Tc present would move with or near the infiltrating water front. Unless there were considerable periods of waterlogging and anaerobic conditions, continued rewetting of the soil would cause the mobile pertechnate anion to move deeper within the soil profile. Once the soluble and non-sorbed ^{99}Tc reached the subsurface horizons with low organic matter, solute flow would continue following the pattern of miscible displacement.

SUMMARY AND CONCLUSIONS

Technetium-99, a long-lived beta-emitting radionuclide, is being produced and released into the environment in increasing quantities from such sources as atmospheric denotations, losses during reactor fuel processing and from increased medical and industrial applications. While there had been relatively extensive studies of ^{99}Tc in animals and humans, there was little information available concerning its behavior in soils and plants at the time this study was initiated. This report then deals with the results of three years of study dealing with the magnitude and mechanisms of ^{99}Tc sorption by soils and uptake by plants.

Results show that ^{99}Tc was sorbed from solution over a period of two to five weeks by 8 of 11 soils studied. The slow rates of sorption and the removal of trace quantities of ^{99}Tc from solution in the presence of large amounts of chloride and phosphate tend to rule out anion exchange as the sorption mechanism. The lack of sorption by low organic matter soils, the reduction following hydrogen peroxide digestion of the soil and high recoveries of sorbed ^{99}Tc on extraction with sodium hydroxide suggest a role for the living and/or non-living organic fraction of the soil. The elimination of sorption following sterilization and increased sorption following addition of dextrose point to a microbial role in the sorption process. However, it has not been established whether this is a direct or indirect role nor is it possible at this time to clearly predict the conditions under which sorption will occur or if sorbed ^{99}Tc is available for plant uptake.

Results of plant uptake studies show that ^{99}Tc can be taken up and translocated into the photosynthetic tissue of higher plants with concentrations in seeds much less than in vegetative tissue. Technetium-99 was also shown to be toxic to plants at low concentrations and evidence suggests that this is a chemically rather than a radiologically induced toxicity. However, this remains to be completely resolved as well as whether there is a threshold level of ^{99}Tc required before toxicity occurs.

In short term, dynamic, and aerobic systems ^{99}Tc will move through soil with characteristic chromatographic and unsaturated miscible displacement patterns. Asymmetrical tailing of the soil CLC distribution of ^{99}Tc will occur in response to unsaturated hydrodynamic dispersion and weak interaction with soil organic matter. This organic matter complexation does not appear to be related to the static, anaerobic, and long term sorption process initially discussed in this report.

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