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Kinetics of ^{99}Tc speciation in aerobic soils

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Graphical Abstract
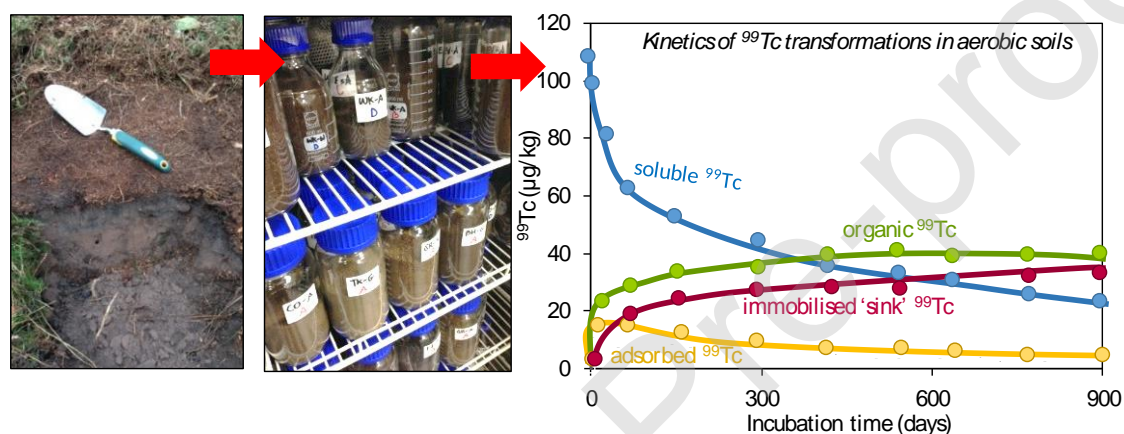
Highlights

- Loss of soluble ^{99}Tc was slow and largely controlled by pH and organic matter

- Steady state conditions were not attained even after 2.5 years incubation

- Complexation with soil humus was key to the progressive ^{99}Tc immobilisation

- Short-term experiments (<2 years) may not reliably predict long-term Tc solubility

ABSTRACT

Technetium-99 is a significant and long-lived component of spent nuclear fuel relevant to long-term assessments of radioactive waste disposal. Whilst ^{99}Tc behaviour in poorly aerated environments is well known, the long-term bioavailability in aerobic soils following direct deposition or transport to the surface is less well understood. This work addresses two questions: (i) to what extent do soil properties control ^{99}Tc kinetics in aerobic soils and (ii) over what experimental timescales must ^{99}Tc kinetics be measured to make reliable long-term predictions of impact in the terrestrial environment. Soil microcosms spiked with ^{99}TcO$_4^-$ were incubated for 2.5 years and ^{99}Tc transformations were periodically monitored by a sequential extraction, which enabled quantification of the reaction kinetics. Reduction in soluble ^{99}Tc was slow and followed a double exponential kinetic model including a fast component enhanced by low pH; a slow component controlled by pH and organic matter, and a persistently soluble ^{99}Tc fraction. Complexation with soil humus was key to the progressive immobilisation of ^{99}Tc. Evidence for slow transfer to an unidentified 'sink' was found, with estimated decadal timeframes. Our data suggest that short-term experiments may not reliably predict long-term ^{99}Tc solubility in soils with low to moderately organic matter contents.

Keywords: technetium; radionuclide; soil; humus; bioavailability

1. INTRODUCTION

Technetium-99 is an artificial radionuclide produced in nuclear reactors by fission of ^{235}U and neutron activation of ^{98}Mo. It has a relatively high fission yield (6.1 %) and a long radioactive half-life (213,000 years) and is, therefore, a significant and long-lived component of spent nuclear fuel and other radioactive wastes (Ashworth and Shaw., 2005; Icenhower et al., 1996, Pearce et al., 2019). In 2016 the UK radioactive waste inventory included 3.87 × 10^{15} Bq of ^{99}Tc, equivalent

to 6.17 tonnes and representing approximately 5‰ of the total radioactivity within the UK radioactive waste stock (NDA, 2017). As a result of its long half-life and its ability to migrate as a soluble anion ($^{99}TcO_4^-$) the long-term environmental impact of ^{99}Tc after geological disposal of radioactive wastes is of considerable interest. In analyses of the implications of a proposed extension to the SFR repository in Sweden, ^{99}Tc consistently appears as one of the most important sources of radiation dose to humans exposed in the terrestrial environment, under several different scenarios, tens of thousands of years after repository closure (SKB, 2014).

Technetium-99 is a groundwater contaminant at some nuclear facilities (Hu et al. 2008) and numerous studies have addressed the migration and plant uptake of ^{99}Tc in the context of groundwater contamination (Ashworth and Shaw, 2005; Murphy and Johnson, 1993). Technetium-99 in groundwater exists predominantly as Tc^{IV}, possibly complexed with soluble or colloidal humic substances (Maes et al., 2004). Even in this form, ^{99}Tc can be brought to the surface by deep-rooted plants (Murphy and Johnson, 1993). Direct contamination of surface soil with ^{99}Tc occurred as result of atmospheric nuclear weapons testing up to 1963 (Tagami and Uchida, 1997) and the Chernobyl accident in 1986 (Uchida et al., 1999). Following direct deposition from the atmosphere or transport to the surface environment from the subsurface, the question arises as to the long-term retention and bioavailability of ^{99}Tc in soils under aerobic conditions. This is important because such contamination may potentially compromise several ecosystem services that soils deliver thereby contributing towards the United Nations Sustainable Development Goals, including provision of food or enhancing biodiversity, among many other key functions (Keesstra et al., 2016).

Despite the expectation that ^{99}Tc in aerobic soils will exist as $^{99}Tc^{VII}$ ($^{99}TcO_4^-$), several studies have shown that its bioavailability in soil-plant systems is reduced with time (e.g. Echevarria et al., 1997). A four-year lysimeter study by Vandecasteele et al. (1989) showed that 70% of ^{99}Tc freshly added to soil as $^{99}TcO_4^-$ was rapidly removed by plant uptake, with a half-time of approximately 50 days. The ^{99}Tc remaining in the (aerobic) plough layer, however, was removed very slowly with an estimated half-time of approximately 30 years, suggesting a kinetically-controlled transformation from bioavailable to recalcitrant form(s). The critical redox

potential for reduction of $^{99}Tc^{VII}$ to $^{99}Tc^{IV}$ is +200 mV at pH 7 (Koch-Steindl and Pröhl, 2001), which is typical of wet but not fully waterlogged soils (Sposito, 2008). Icenhower et al. (2009) have concluded that it is the availability of reducing agents, including organic matter and surface-sorbed Fe(II), which controls the reduction of Tc^{VII} to Tc^{IV}, rather than the bulk redox environment.

In assessments of radioactive waste disposal, long-term predictions of ^{99}Tc availability for plant uptake and human exposure are needed for a range of scenarios. Soils with wide-ranging properties provide a spectrum of physico-chemical characteristics which may render ^{99}Tc either highly bioavailable or highly immobile, even under the typically aerobic conditions which are conducive to plant growth and crop production. Existing databases of solid-liquid distribution coefficients for ^{99}Tc provide a starting point for making exposure and risk calculations, but these data are often based on relatively short-term experiments and relatively small numbers of measurements (Gil-García et al., 2009). In this study our aim was to address two questions: (i) to what extent do easily-measurable soil properties control the kinetics of ^{99}Tc speciation changes in aerobic soils and (ii) over what experimental timescales must we measure Tc reaction kinetics in order to make reliable long-term predictions of ^{99}Tc impact in the terrestrial environment?

2. MATERIALS AND METHODS

2.1. Soil sampling

Twenty topsoil samples (0–15 cm depth) were collected from a number of locations in the UK (Table 1, Fig. S1) covering a broad range of relevant soil characteristics including pH, texture, organic carbon content, land use and parent material. When possible, soils developed in the same parent material but under different land uses (e.g. arable or grassland versus woodland) were collected. Four or five sub-samples were collected within a ~5 m^2 grid and combined to form a composite sample of ~3 kg field moist soil. The field moist soil was homogenised and air dried at room temperature until just dry enough to be sieved to <4 mm. The soils were not allowed to dry completely so as to maintain microbial activity. After sieving, soils were kept in polythene bags

at 4°C to preserve their remaining moisture content without allowing anaerobic conditions to develop.

2.2. Soil characterisation

Approximately 30 g of each soil were oven dried (105°C) and ground in an agate ball-mill to produce a fine homogeneous powder for acid digestion and total element analysis. Soil digestion was undertaken by weighing 0.20 g $\pm$ 0.01g of soil into a Savillex™ vial, adding concentrated *Primar* grade HNO_3 (4 mL) and heating at 80°C overnight to pre-digest the organic matter present in soils. This was followed by addition of concentrated *Primar* grade HF (2.5 mL), HNO_3 (2 mL) and $HClO_4$ (1 mL) and heating overnight to 160°C using a stepped heating program to digest silicate and oxide phases. The dry residue was re-constituted by warming with 2.5 mL ultrapure water and 2.5 mL HNO_3; the final volume was made up to 50 mL with ultrapure water (18.2 MΩ cm). Three standard reference materials (NIST SRM 2711a *Montana Soil*, NIST 1646a *Estuarine Sediment* and IRMM BCR-167 *Estuarine Sediment*) were digested in duplicate and five reagent blanks were prepared in an identical manner to check the accuracy and precision of the digestion and analysis methods. Elemental recoveries were typically >80% for the majority of the certified elements. All the soil digests and reagent blanks were diluted 1-in-5 before analysis by ICP-MS.

Soil pH was determined by shaking 10 g of sieved soil with 0.01 M $CaCl_2$ at a liquid to solid ratio of 2.5 L kg^{-1} for 30 minutes. Organic carbon (OC) contents were determined in finely ground material using a FLASH EA1121 CNS analyser. Total free iron oxides (Fe_{OX}, Al_{OX} and Mn_{OX}) in soils were extracted by shaking ca. 0.25 g finely ground soil with 20 mL of 0.3 M Na-citrate in 1 M $NaHCO_3$ and 0.07 M Na-dithionite for 24 h in a 20°C water bath followed by centrifugation and filtering to <0.22 μm. Estimates of amorphous and poorly crystalline oxides (Fe_{AM}, Al_{AM} and Mn_{AM}) were obtained following extraction in 0.2 M ammonium oxalate and 0.125 M oxalic acid, shaken in darkness for 2 h following a method adapted from Schwertmann (1973). All filtered solutions (<0.2 μm) were acidified to 2% HNO_3 and diluted 1-in-100 before analysis by ICP-MS.

2.3. Soil incubation

Soil preparation, ^{99}Tc addition, incubation setup, microcosms

Tc-99 solution (3970 kBq, 5 mL of $NH_4{}^{99}TcO_4$ in H_2O) was obtained from High Technology Sources Ltd. This primary stock was diluted with ultrapure water to produce a solution containing 62.6 mg L^{-1} ^{99}Tc that was used to contaminate soil to be incubated in microcosms (initial background concentrations of ^{99}Tc in all soils were zero).

Portions of ~2 kg (on a dry soil basis) of partially air-dried soils were weighed and the moisture contents were readjusted with ultrapure water. No attempt was made to achieve a pre-determined water content; rather, a friable but moist consistency was sought to aid soil mixing, which required different volumes of water to be added to individual soils. The volume of water added to each soil was recorded. The soils were then placed in an incubator at 10°C and allowed to equilibrate for 23 days. This pre-incubation step was to avoid including the short-lived 'flush' of microbial activity when the soils were initially moistened as part of the Tc incubation period; it was felt that this could distort the pattern of ^{99}Tc dynamics. After this period, a portion of ~250 g soil was removed and transferred to 0.5 L Duran bottles to be used as control soils (and for further short-term experiments), whilst the remaining soil was amended with the equivalent of 108 μg ^{99}Tc kg^{-1} dry soil. To this end, approximately 2.8 mL of the ^{99}Tc solution were slowly added to each soil while the samples were mechanically stirred (c. 60 rpm) with the aid of a food mixer for 4 minutes to ensure uniform contamination with ^{99}Tc.

The Tc-amended soil was distributed equally between three Duran bottles of 1 L capacity as individual microcosms. The bottles had one single hole in the lid to allow gas exchange and to prevent anaerobic conditions developing whilst avoiding excess water loss during incubation. The soil weights for each microcosm (~500 g dw) were recorded so the dry soil mass could be estimated and the moisture content could be monitored throughout the experiment. The spiked and control microcosms were incubated in darkness at 10.0 ± 1.0°C for 897 days. The microcosms

were regularly shaken by hand to aid aeration. During periodic extractions of the soils, soluble Mn and Fe was monitored in all soils as indicators of any redox changes.

Microcosm sampling and sequential extractions

Microcosms were sampled periodically between initial contamination and final sampling at 897 days. The frequency of sampling was high (average of approximately 0.5 day) over the first 5 days (see Section 2.4) then reduced to an average of approximately 50 days for the remainder of the experiment. Physico-chemical transformations of ^{99}Tc in each soil during incubation were periodically monitored by means of a sequential extraction procedure (Table 2) based on the methods developed by Zhao and McGrath (1994) for sulphate and Shaw et al. (2019) for iodine. At each sampling time, a portion of soil equivalent to 4.0 ± 0.01 g dry soil was transferred from each microcosm to a 50 mL PE centrifuge tube and then subjected to a three-step sequential extraction procedure devised to quantify: (i) soluble, (ii) specifically adsorbed and (iii) organically bound ^{99}Tc pools in each soil. First, soluble ^{99}Tc (^{99}Tc$_{sol}$) was extracted with 20 mL 0.01 M KNO$_3$ (intended to mimic soil pore water composition) for 16 h using an end-over-end shaker. This was followed by further equilibration with 20 mL 0.16 M KH$_2$PO$_4$ for 16 h to extract specifically adsorbed ^{99}Tc (^{99}Tc$_{ads}$). At the end of each step the soil suspensions were centrifuged at 3500 rpm for 30 min, the supernatant solutions filtered through 0.22 μm syringe filters and divided into four equal aliquots. Two aliquots, stabilised with 2% HNO$_3$ and 1% TMAH respectively, were used to determine total ^{99}Tc concentrations within the extracts, whilst a third aliquot was immediately used for speciation analyses (described below). The remaining solution was kept at 4°C for DOC analysis. The third step of the sequential extraction involved heating the soils with 10% tetra methyl ammonium hydroxide (TMAH) solution at 90°C for 14 h to dissolve organically bound ^{99}Tc (^{99}Tc$_{org}$) linked to humic and fulvic acids. These suspensions were centrifuged at 3500 rpm for 30 min and a 1 mL aliquot was further diluted to give a final concentration of 1% TMAH for analysis. Only total ^{99}Tc analyses were undertaken using the TMAH extracts. The residual soil samples were weighed between extractions to account for carryover of the previous extractant and to calculate the total solution volume present at each stage. The difference between the

combined sequentially extractable concentrations of ^{99}Tc and the total ^{99}Tc added enabled estimation of non-extractable ^{99}Tc (designated ^{99}Tc$_{sink}$) remaining in the soil.

2.4. Assessing short term Tc dynamics

The short term (<5 days) dynamics of soluble ^{99}Tc in soils was investigated using sub-samples from the control soils. In order to keep the liquid-to-solid ratio as close as possible to 5 L kg^{-1} throughout all the extractions, the study of the short term dynamics was undertaken in two independent experiments.

To investigate ^{99}Tc behaviour during the first 3.5 h after addition to the soils, a moist mass of each control soil equivalent to 6 g dry weight was weighed into 50 mL PE centrifuge tubes in triplicate and 31 mL of 0.01 M KNO$_3$ were added. An air-filled head space (~15 mL) was deliberately left to maintain an aerobic environment. An aliquot (2 mL) of 0.01 M KNO$_3$ solution containing 0.6 µg ^{99}Tc was added to the soil suspensions which were then shaken end-over-end for 3.5 hr at room temperature. Samples of the supernatant (2.0 mL) were then taken after 0.5, 1, 2 and 3.5 h, following centrifugation of suspensions at 3800 rpm for 4 min, and filtered to <0.22 µm. The filtered samples were then split into two aliquots: 0.5 mL were transferred to a glass vial containing 19.5 mL ultrapure water for DOC analysis whilst the remaining aliquot was transferred to an ICP tube containing 4 mL 1% TMAH for further analysis. After each sampling, the soil suspensions were disaggregated with a vortex mixer and return to the shaker immediately.

To study ^{99}Tc behaviour during the first five days of contact with the soils, an identical procedure as above was followed using another set of sub-samples from control soils. In this experiment the soil suspensions were sampled 6, 21, 46, 75, 100 and 123 hr after addition of ^{99}Tc.

2.5. Analyses of solutions

Total concentrations of Tc

Samples were analysed using an iCAP-Q ICP-MS (Thermo Fisher Scientific, Bremen, Germany) instrument. When analysing ^{99}Tc by mass spectrometry isobaric interference may be encountered from ^{99}Ru (13% isotopic abundance) as well as polyatomic interferences from Mo hydride ($^{98}Mo^1H^+$, 24% abundance) and a range of K-based polyatomic species such as $^{40}Ar^{41}K^{18}O$, $^{41}K_2^{17}O$ and $^{41}K^{40}K^{18}O_9$. However, operating the instrument with a collision-cell (Q cell), using He with kinetic energy discrimination, was found to remove spectral interferences successfully, enabling accurate ^{99}Tc measurements while maintaining a sensitivity of 70-80 kcps ppb^{-1}. Further details on the analytical method and ICP-MS settings can be found in the Supplementary Information.

Samples were introduced from an autosampler (Cetac ASX-520) incorporating an ASXpress™ rapid uptake module through a perfluoroalkoxy (PFA) Microflow PFA-ST nebuliser (Thermo Fisher Scientific, Bremen, Germany). Internal standards were introduced to the sample stream on a separate line via the ASXpress unit and included Ge, Rh (10 µg L^{-1}) and Ir (5 µg L^{-1}) in 2% trace analysis grade (Fisher Scientific, UK) HNO$_3$ and Re and Ir (5 µg L^{-1}) in 1% TMAH. Peak dwell times were 10 mS for most elements with 150 scans per sample. Sample processing was undertaken using Qtegra™ software (Thermo-Fisher Scientific) utilizing external cross-calibration between pulse-counting and analogue detector modes, when required. The Radioactive Standard NIST SRM 4288B (31.55 kBq g^{-1}, 5mL of $^{99}TcO_4^-$ in 0.001M KOH) was diluted with ultrapure water to produce 100 mL of standard solution with a concentration of 2493 µg L^{-1} $^{99}TcO_4^-$, which was used for calibration (0.5, 1, 5, 10 and 25 µg L^{-1}). Other elements relevant to understanding Tc sorption were also measured, including major cations, such as Fe and Mn, and trace elements.

Solution speciation

Speciation analysis was undertaken by IC-ICP-MS following in-line chromatographic separation using a Dionex ICS-3000 fitted with a 50 mm length PRP-X100 Hamilton anion

exchange column. Development of an ion chromatographic method for adequate separation of ^{99}Tc species within a reasonable transit time was attempted. A number of potential mobile phase compositions and conditions were tested, as reported in the Supplementary Information. Following an optimisation process, the selected mobile phase consisted of isocratic elution with 0.05 M NH$_4$ClO$_4$ solution at 1.5 mL min^{-1}. The Radioactive Standard NIST SRM 4288B, diluted as described above, was used as a pertechnetate standard for calibration (1, 5 and 20 μg L^{-1}). Sample processing was also undertaken using Qtegra™ software (Thermo-Fisher Scientific) by manual integration of peaks. Instrumental drift was addressed by analysing ^{99}Tc calibration standards every 12 samples.

2.6. Statistical analysis

Statistical analyses of data, including linear regression and testing of statistical significance, were undertaken using the RStudio software package (v.1.1.383, RStudio, Inc). Significance testing of model fits is described in Supplementary Material (Tables S1 and S2).

2.7. Modelling ^{99}Tc kinetics

Time-dependent reductions in ^{99}Tc$_{sol}$ concentrations could be described using a dual rate, double exponential model with an 'offset' representing a persistently soluble fraction (Eq 1):

$$Tc_{sol}(t) = A.e^{-tk_{fast}} + B.e^{-tk_{slow}} + C \qquad \text{(Eq 1)}$$

where $Tc_{sol}(t)$ is the soluble ^{99}Tc concentration at any time, t, after initial contamination of the soils, A and B are the initial ^{99}Tc concentrations (μg kg^{-1}) in solution subject to 'fast' and 'slow' depletion, respectively, and C is the ^{99}Tc concentration persistently remaining in solution. The first-order rate coefficients k_{fast} and k_{slow} (t^{-1}) represent 'fast' and 'slow' rates of depletion of A and B, respectively. This model was fitted to experimental data from each soil using the Solver function in Microsoft Excel®; during fitting the sum of $A+B+C$ was constrained to a value of 108 μg kg^{-1} which was the total initial concentration of ^{99}Tc added to each soil at the beginning of the experiment. We attempted to fit other analytical models, including simple first order and spherical

diffusion models, to experimentally measured $^{99}Tc_{sol}$ concentrations but Eq 1 consistently provided the best fits to data from all soils (see Fig. S2).

The kinetics of $^{99}Tc_{org}$ (TMAH-extractable) accumulation in soil could be described using a dual rate 'ingrowth' model (Eq 2):

$$Tc_{org}(t) = \frac{R_1}{k_1}(1 - e^{-tk_1}) + \frac{R_2}{k_2}(1 - e^{-tk_2}) \qquad\qquad (Eq\ 2)$$

where $Tc_{org}(t)$ is the TMAH-extractable ^{99}Tc concentration at any time, t, after initial contamination of the soils, R_1 and R_2 are fast and slow rates, respectively, of $^{99}Tc_{org}$ formation and k_1 and k_2 (t^{-1}) are fast and slow rate coefficients, respectively, of $^{99}Tc_{org}$ 'loss' after formation.

3. RESULTS

3.1. Soil characterisation

The general properties of the soils used in this study are reported in Table 1. Organic carbon contents (OC) varied from 1.7 – 38.6% strongly reflecting land use and dominant vegetation at the sampling sites. Soil pH ranged between 3.4 – 8.0, with the lowest values reported for a woodland soil (BY-W) overlying pyrite-rich bedrock and the highest values for calcareous soils (SR-W, SR-A, WS-A) with inorganic C up to 5%. The concentrations of free oxides spanned four orders of magnitude, ranging from 1,180 to 22,700 mg kg^{-1} across the 20 soils examined. The broad ranges reported above reflect the diverse parent materials and land uses of the sites from which soils were collected, which included arable, grassland, woodland and moorland.

3.2. Soluble Tc ($^{99}Tc_{sol}$)

Short term dynamics (<5 days)

The ^{99}Tc initially added to the soils as pertechnetate ($^{99}TcO_4^-$) remained largely soluble in most soils within the first few hours after addition (Fig. 1a and 2). Earlier studies have shown

that $^{99}TcO_4^-$ is poorly adsorbed on soils or sediments under aerobic conditions during short-term batch experiments (Palmer and Meyer, 1981; Van Loon, 1986). However, evidence for removal of ~30% $^{99}Tc_{sol}$ was found for peaty acidic soils (DY-M, WK-W) within 0.5 hr of addition (Fig. 2). Changes in the soluble concentration of ^{99}Tc over time indicate that short-term transformations are largely governed by soil properties (Fig. 1 and 3). For example, in arable soils (2–4% OC) ^{99}Tc remained mostly soluble, whilst up to 33% loss of soluble ^{99}Tc was observed in grassland soils (5–11% OC) 5 days after Tc addition. For woodland and moorland soils (5–39% OC) the loss of $^{99}Tc_{sol}$ reached 50% within 5 days in acidic soils. However, a minor loss of 5–11% was noted for 2 woodland soils (BH-W and SR-W), which were collected from immature woodlands developed over limestone bedrock (Fig. 3). The above observations indicate that the decline in $^{99}Tc_{sol}$ in this period was primarily controlled by both OC and pH.

Long term ^{99}Tc dynamics (5-897 days)

For all of the soils in the long-term experiment, a proportion of ^{99}Tc was found to remain in a soluble form throughout the 2.5 yr incubation period (Fig. 1a), probably due to pertechnetate being the most stable species under aerobic conditions and over a broad pH range (Shaw et al., 2004). However, a general decline in $^{99}Tc_{sol}$ throughout the experiment was observed in all cases, with substantial differences between soils (Fig. 3). After 1 year, removal of $^{99}Tc_{sol}$ from solution ranged between 6 – 73% and this increased to 25 – 95% following incubation for 2.5 yr. As shown in Fig. 3, only acidic, organic-rich soils (OC >11%; e.g. DY-M) appeared to be close to a steady state with respect to $^{99}Tc_{sol}$ whilst the remaining soils were still losing soluble $^{99}Tc_{sol}$ at a slow rate after 2.5 years.

Long term time-dependent transformations of ^{99}Tc also appear to be strongly governed by soil properties. Specifically, soil pH and OC were found to play a major role in controlling both the extent and the rate of these transformations (Fig. 2). Regression analyses suggested that the long term dynamics of $^{99}Tc_{sol}$ can be principally explained (70 – 75%) by pH and C_{org}, whilst the role of other potential binding surfaces such as Fe, Mn or Al oxy-hydroxides is marginal, explaining <7% of the variation in $^{99}Tc_{sol}$. Thus, ^{99}Tc largely remained in soluble forms in most arable and

grassland soils, with a consistent but slow decline throughout the experiment (Fig. 1a and 3). Total $^{99}Tc_{sol}$ loss after 2.5 yr ranged between 22% for a calcareous arable soil (SR-A) to 95% for a peat-rich grassland, soil (DY-G), although most values were in the range 40 – 50%. Abdelouas et al., (2005) reported a 30% loss of soluble ^{99}Tc in an aerobic soil with 18% organic carbon after 26 days, whereas no apparent loss of $^{99}Tc_{sol}$ occurred until 72 days when soil organic carbon concentrations were <6%.

By contrast, sorption and migration of $^{99}Tc_{sol}$ into non-soluble pools were the dominant processes in the majority of the studied woodland and moorland soils. A substantial drop in $^{99}Tc_{sol}$ (15 – 77% loss of total ^{99}Tc added) was seen within 49 days in these soils (Fig. 1-3). This was followed by a slower additional loss of $^{99}Tc_{sol}$ over the following months, reaching a maximum of 95% in soil DY-M. Thus, in organic, acidic soils only 5 – 20% of the added ^{99}Tc remained soluble 2.5 years after initial contamination of the soils. However, for *calcareous* woodland soils approximately 65% of initially added ^{99}Tc remained soluble at the end of the experiment.

Changes in the speciation of $^{99}Tc_{sol}$

Speciation analysis following chromatographic separation indicated that there were no statistically significant differences between $^{99}Tc_{sol}$ and $^{99}TcO_4^-{}_{sol}$ concentrations across the dataset (Fig. S3). Thus, pertechnetate was the dominant species in the soil solution for all soils throughout the incubation. This observation is of key radioecological relevance given that pertechnetate can be transported at 90% of groundwater velocity in aquifers (Icenhower et al., 2009) and is the only Tc species that can be taken up by plants in appreciable amounts (Van Loon, 1986) thus having significant potential to enter the food chain. However, speciation analyses also revealed some evidence for the transformation of pertechnetate in the incubated microcosms, in the form of consistent but unidentified peaks, with a strongly pH-dependent morphology, in the chromatograms of Tc_{sol}. The concentrations of these unknown ^{99}Tc species in solution remained <1 µg kg^{-1} (< 1% total Tc) throughout the experiment.

For acidic and near-neutral soils, a series of three consecutive, but partially overlapping, sharp peaks (Fig. 4) with short column retention times (12–50 seconds) were present from as

early as 4 days incubation. The concentrations increased over time to asymptotes of 0.02 – 1.1 µg kg^{-1} at 200 days. The very short transit times through the chromatographic column indicate that the newly formed $^{99}Tc_{sol}$ species emerged along with the mobile phase suggesting virtually no retention by the anion exchange resin. This may be attributed to the occurrence of ^{99}Tc in cationic or neutral forms, such as the sparingly soluble $^{99}Tc^{IV}O_2 \cdot nH_2O_{aq}$, following reduction of $^{99}Tc^{VII}$ to $^{99}Tc^{IV}$, which is likely in acidic, high organic soils as Eh-pH diagrams suggest (Takeno, 2005). Enhanced solubility of $^{99}Tc^{IV}O_2 \cdot nH_2O_{aq}$ through formation of polymers or colloids has been reported (Maes et al. 2004). Formation of cationic species such as $^{99}Tc^{(IV)}O(OH)^{+}$, following reduction, could also account for the poor affinity for the resin although Tc stability diagrams (Takeno, 2005) suggest this would only be likely in highly acidic soils. Complexation of reduced ^{99}Tc with organic ligands is known to enhance solubility (Maes et al., 2004) and the DOC concentrations measured in the KNO$_3$ extracts (up to 1600 mg kg^{-1}) suggest that formation of organic complexes including $^{99}TcO(OH)–HA$ and $^{99}TcO(OH)_2–HA$ is possible (Boggs et al., 2011). However it is unlikely that the rapidly emerging unknown peaks reflect these water soluble humic complexes given their negatively charged nature.

Peak broadening and tailing in chromatograms were observed with increasing soil pH (Fig. 4) suggesting co-elution of a number of pH-controlled species. Technetium extracted from calcareous soils displayed a distinctive broad peak with longer retention times (40–50 sec) suggesting that pH>7 could lead to formation of Tc species such as carbonate complexes. The presence of carbonate ligands in groundwater has been reported to enhance the formation of soluble $^{99}Tc^{IV}–$carbonate complexes (Wildung et al., 2000) which can be an important transport pathway. $^{99}Tc^{IV}(CO_3)(OH)_{2\ aq}$ is thought to be the main species in bicarbonate media over a large range of chemical conditions and it is predicted to be stable across a wide pH range from 2 – 8 at high P_{CO2}, whilst $^{99}Tc^{IV}(CO_3)(OH)_3^{-}{}_{aq}$ dominates at pH > 8 (Alliot et al., 2009). However, this species is not expected to be dominant in soils with low P_{CO2}.

Modelling $^{99}Tc_{sol}$ kinetics

Removal of ^{99}Tc from solution was found to conform to a dual rate, double exponential model (Fig. 1a and 3). Pearson correlation coefficients (r) for model fits (see Table S1) and comparison between observed and modelled ^{99}Tc$_{sol}$ for all soils within the dataset (Fig. S2) showed that the model accurately fitted the experimental data throughout. Even for the weakest model fits, for the arable soils, SR-A (r=0.543) and WK-A (r=0.448), the significance of the fits was >99.99% (Table S1) indicating that ^{99}Tc$_{sol}$ declined significantly with time in all soils. Greater scatter of points around the line of unity in Fig. S2 was seen for higher concentrations of ^{99}Tc$_{sol}$ - i.e. at shorter incubation times before substantial removal of ^{99}Tc from soil solution had occurred. Thus, the model fit to the experimental data was generally closer over longer incubation times. Significant correlations between the kinetic parameters (*A*, *B*, *C*, k_{fast} and k_{slow}) and soil properties were found (Table 3 and Fig. S4-S5). Strong positive relationships between pH and model parameters A and C indicate that soil pH played a key role throughout the experiment, controlling the rapid 'fixation' of ^{99}Tc at the earliest stage of the incubation and the persistently soluble ^{99}Tc remaining after 897 days. Lower pH appeared to enhance rapid depletion of ^{99}Tc$_{sol}$ (as measured by parameter *A*) at the expense of lower residual ^{99}Tc$_{sol}$ (indicated by parameter *C*, Table 4).

It is worth noting that model fits for soils with pH>6.8 yielded *A*=0 (and thus k_{fast}=0) so that these soils conformed to a single exponential model controlled by slow removal of ^{99}Tc from solution (k_{slow}) (Fig. 3).

Depletion period

The 'slow' rate coefficient of ^{99}Tc$_{sol}$ depletion in Eq. 1 (k_{slow}) was used to estimate the time required to deplete 99% of the soluble Tc fraction (Eq. 3):

$$T_{99} \, (days) = \frac{ln(100)}{k_{slow}} \qquad \text{(Eq. 3)}$$

where k_{slow} (t^{-1}) is the first-order rate coefficient representing the 'slow' rate of depletion of *B*. Thus, the parameter T_{99} provides an indication of the time taken for Tc$_{sol}$ to approach the persistently soluble concentration, *C*, which is probably still subject to slow removal from solution

but which is not observable in many soils on an experimental timescale of less than a decade or more. T_{99} ranged between 1.1 and 27.0 yr and showed a clear relationship with land use: increasing soil OC contents from arable (median T_{99} = 6.3 yr) to grassland (median T_{99} = 3.9 yr) to woodland (median T_{99} = 3.5 yr) shortened the timeframe needed to reduce the $^{99}Tc_{sol}$ fraction B to 1% (Fig. 5). A strong, significant relationship between T_{99} and B indicates that the depletion period is also controlled by the size of the pool to be slowly removed (Table 3). Soluble ^{99}Tc in only 6 soils appeared to approach C within or very close to the incubation timeframe (≤2.7 yr after contamination with $^{99}Tc_{sol}$).

3.3. Specifically adsorbed Tc ($^{99}Tc_{ads}$)

Phosphate competes strongly with anions specifically adsorbed by Fe, Al and Mn oxide surfaces in soils and so methods utilizing competition with phosphate have been used to estimate, for example, plant-available sulphate and selenite (Stroud et al., 2012). It is reasonable to assume that phosphate will exchange with other oxyanionic species, such as pertechnetate, which are weakly adsorbed in a similar way to selenate and sulphate. Speciation analysis indicated that pertechnetate ($^{99}TcO_4^-{}_{ads}$) was the dominant phosphate-extractable species ($^{99}Tc_{ads}$) for all soils throughout the long-term incubation (Fig. S3).

The $^{99}Tc_{ads}$ fraction remained relatively small and did not exceed 15% of the total ^{99}Tc throughout the incubation period. Soil properties appear to control the maximum concentrations of $^{99}Tc_{ads}$ (Fig. 1b and 6a). For arable and grassland soils, changes in $^{99}Tc_{ads}$ over time followed a distinctive trend, gradually rising following addition of ^{99}Tc, peaking at 200 – 400 days (up to 9 µg kg^{-1}) and subsequently stabilising or declining very slowly for the remainder of the experiment. Acidic, organic-rich woodland and moorland soils showed greater concentrations of $^{99}Tc_{ads}$ and more rapid transfer of $^{99}Tc_{sol}$ to $^{99}Tc_{ads}$, reaching a maximum concentration of 16 µg kg^{-1} of $^{99}Tc_{ads}$ (15% of total added) at ca. 200 days before starting to decline thereafter. There were generally weak correlations between the formation of $^{99}Tc_{ads}$ and the abundance of potential sorption surfaces, including Al, Mn and Fe oxides, which may reflect the complexity of Fe-^{99}Tc interactions.

3.4. Organically bound Tc ($^{99}Tc_{org}$)

$^{99}Tc_{org}$ kinetics

The organic (TMAH-extractable) pool of ^{99}Tc ($^{99}Tc_{org}$) varied widely across all soils and throughout the experiment, ranging from 2 to 70 µg kg^{-1} which accounted for 2 – 65% of the added ^{99}Tc (Fig. 1c). Up to 25 µg kg^{-1} $^{99}Tc_{org}$ (c. 23%) was measured as early as 4 days after spiking highly organic soils indicating that Tc can undergo rapid transformation to organic forms in soils. Changes in $^{99}Tc_{org}$ over time reflected land use and soil characteristics, with the extent of the transformations strongly influenced by both pH and OC (Fig. 6b). For low to moderately organic, arable and grassland soils, the incorporation of $^{99}Tc_{sol}$ into the organic pool slowly increased over time and appeared to reach an asymptote at 400 days (Fig. 1c). Median $^{99}Tc_{org}$ concentrations observed were 2–30 µg kg^{-1}; thus up to 30% of the total ^{99}Tc originally added was organically bound after 900 days. Evidence for faster reaction rates was found for acidic woodland soils in which high organic carbon and low pH enhanced $^{99}Tc_{org}$ formation. As shown in Fig. 1c, $^{99}Tc_{org}$ increased most rapidly within the first 200-300 days in these soils, after which the rate of increase reduced in accordance with Equation 2.

Modelling $^{99}Tc_{org}$

A dual rate 'ingrowth' model (Eq. 2) was fitted to data showing accumulation of $^{99}Tc_{org}$ over time (Fig. 1c). Pearson correlation coefficients (r) for model fits (Table S2) for all soils within the dataset showed that the model accurately fitted the experimental data throughout. Even for the weakest model fit, grassland soil TK-G (r=0.606), the significance of the fits was >99.99% (Table S2) indicating that $^{99}Tc_{org}$ increased significantly with time in all soils. The comparison between observed and modelled $^{99}Tc_{org}$ for the full dataset showed slightly greater scatter around the line of unity than was observed for the model describing $^{99}Tc_{sol}$ kinetics (Fig. S2). This probably reflects the complexity of ^{99}Tc transformations through a range of processes with different dependencies on soil characteristics. A weak yet significant correlation between pH and the 'fast' rate coefficient (k_1) was observed (Table 3, Fig. S6). Strong and significant relationships between

the kinetic parameters describing change in $^{99}Tc_{sol}$ and $^{99}Tc_{org}$ indicate that both reservoirs are closely connected (Table 3, Fig. S7).

3.5. Inaccessible Tc ($^{99}Tc_{sink)}$

A variable though consistent increase in $^{99}Tc_{sink}$ was observed for the majority of soils during the course of the long-term experiment (Fig. 1d); concentrations of $^{99}Tc_{sink}$ broadly reflected OC and, to a lesser extent, pH as the data in Fig. 6c suggest. Thus, for arable and grassland soils, $^{99}Tc_{sink}$ slowly increased over time and only up to 20% of the added ^{99}Tc was immobilised after 900 days. Greater OC contents in woodland soils enhanced the formation of $^{99}Tc_{sink}$ (Fig. 1d); an initially sharp increase to 20 µg kg^{-1} within the first 50 days was followed by a slower increase over time, reaching up to 40 µg kg^{-1} at 900 days. By the end of the experiment, between 13 – 40% of the added $^{99}Tc_{sol}$ was present in recalcitrant forms across all soils studied, becoming progressively inaccessible to the extraction methods we used.

4. DISCUSSION

Short term ^{99}Tc dynamics

The rapid drop in $^{99}Tc_{sol}$ following initial contamination reflects a range of processes operating simultaneously. Abiotic mechanisms include electrostatic interactions occurring almost instantly and largely controlled by pH, which is supported by the strong negative relationship observed between the modelled kinetic parameter *A* (i.e. the fraction of $^{99}Tc_{sol}$ subject to rapid removal from solution) and soil pH. However, in general, anions are poorly sorbed in soils due to low abundance of anion exchange sites. Statistical analysis of our data suggested that Fe/Mn/Al oxy-hydroxides play a minor role in $^{99}Tc_{sol}$ behaviour, which is consistent with the literature. Pertechnetate is known to adsorb only weakly onto mineral surfaces. Kaplan (2003) and Abdelouas et al. (2005) reported no pertechnetate sorption on mineral particles including quartz, clays and calcite in three sterilised soils. Previous studies detected only marginal sorption on Fe, Al and Mn oxides as well as a range of clays among other silicates (Palmer and Meyer, 1981).

The $^{99}Tc_{ads}$ pool remained <20% of the initially added ^{99}Tc throughout the experiment. Such low $^{99}Tc_{ads}$ alongside the rapid decline in $^{99}Tc_{sol}$ provides strong evidence that abiotic, surface-charge mediated adsorption on sesquioxides is limited and loss of $^{99}Tc_{sol}$ is largely due other mechanisms.

Our observations indicate that ^{99}Tc has a strong affinity for OC. Fast $^{99}Tc_{sol}$ to $^{99}Tc_{org}$ transfers following contamination strongly suggest that Tc rapidly sorbs onto humus. Carboxyl groups on humic surfaces may be protonated, therefore less negatively charged, at low pH thus reducing repulsion and potentially enabling some degree electrostatic sorption. However it is highly likely that ^{99}Tc sorption or incorporation to organic matter is the result of more complex mechanisms largely driven by the rapid reduction of pertechnetate enhanced by organic groups (e.g. hydroquinones), followed by binding to aromatic carbon. Reduction of $^{99}Tc^{VII}$ in humic-rich environments has been reported to form $^{99}Tc^{IV}$ and $^{99}TcO_2 \cdot nH_2O$ associated with humic substances in the solid phase (Maes et al., 2004); there is also evidence for $^{99}Tc^{IV}$ forming binuclear complex compounds with carboxyl ligands of organic matter (Maes et al., 2004). Different $^{99}Tc_{sol}$ to $^{99}Tc_{org}$ transfer rates following contamination may reflect differences in the composition and chemistry of humic substances present in soils, which will result in substantially different densities of functional groups and therefore different binding capacities. This has been known for some time but the mechanisms responsible have not been fully elucidated due to the complexity and variability of humic substances (De Paolis and Kukkonen, 1997). The positive correlation of OC with A (rapidly removed fraction of $^{99}Tc_{sol}$) indicates that OC, in conjunction with low pH, accelerates transfer of soluble $^{99}Tc_{sol}$ into the organic reservoir. The close interplay between $^{99}Tc_{sol}$ and $^{99}Tc_{org}$ is further illustrated by positive relationships between A from Eq. 1 and R_1 and R_2 from Eq. 2, indicating that greater proportions of rapidly removed $^{99}Tc_{sol}$ (A) result in faster rates of formation of $^{99}Tc_{org}$ (R_1 and R_2) (Fig. S7).

The literature suggests that biological reduction of Tc^{VII} to Tc^{IV} in nature is a slow process even under low E_h conditions (Icenhower et al. 2009). Therefore it is reasonable to assume that the ^{99}Tc behaviour within the first hours following contamination is primarily abiotically driven. However, it is highly likely that other processes with a biotic component, such as enzymatic

activities, may also operate. Thus, the presence of reactive enzymes in soils may result in rapid removal of $^{99}Tc_{sol}$ and direct $^{99}Tc_{sol}$ to $^{99}Tc_{org/sink}$ transfers through enzymatic $^{99}Tc^{VII}$ reduction and subsequent $Tc^{IV}O_2 \cdot nH_2O$ formation. This could contribute to the rapid formation of $^{99}Tc_{org}$ and $^{99}Tc_{sink}$ observed during the initial stages of the incubation experiment.

It is generally recognised that reduction reactions in soils are enhanced at lower pH and that enzyme activity is greater in soils with large humus concentrations. Thus the immediate removal of $^{99}Tc_{sol}$ appears to be marginal in soils with pH>6.8. The absence of a fast component in the model (Eq. 1) fits for calcareous soils indicate that $^{99}Tc_{sol}$ transfer to sorbed forms is primarily dominated by slow kinetics in these soils. Therefore, high pH in conjunction with relatively low organic carbon (OC<7.5%) produced relatively low rates of ^{99}Tc fixation. This is of key environmental relevance given that rendzina soils overlying karstified calcareous terrains would be inefficient in retaining deposited ^{99}Tc and would not prevent transport, dispersion and discharges to the underlying aquifer.

Long term ^{99}Tc dynamics

Electrostatic adsorption onto Fe, Mn and Al oxides apparently played a minor role throughout the experiment. Low pH increased the transfer of $^{99}Tc_{sol}$ to $^{99}Tc_{ads}$, which peaked during the first few months of the experiment. This was followed by a slower decline in $^{99}Tc_{ads}$, probably associated with active transfer to the $^{99}Tc_{org}$ and $^{99}Tc_{sink}$ pools. There are no long-term binding mechanisms for pertechnetate; for ^{99}Tc to become strongly adsorbed a change in Tc speciation must occur. Pertechnetate can be removed from solution ($^{99}Tc_{sol}$) or desorbed from weak sorption sites ($^{99}Tc_{ads}$) through reduction to $^{99}Tc^{IV}$ and formation of the sparingly soluble $^{99}Tc^{IV}O_2 \cdot nH_2O$, the most common $^{99}Tc^{IV}$ species that is stable across the pH range encountered in soils. Reduction can occur through a number of mechanisms and, specifically, the ability of microorganisms to reduce Tc has been well documented in the literature. Comparative studies conducted on sterilised and non-sterilised batches of soil have demonstrated the crucial role of bacterial populations in ^{99}Tc speciation and immobilisation (Abdelouas et al., 2005; Burke et al., 2005). The most

extensively documented mechanism is direct enzymatic reduction of $^{99}TcO_4^-$ by anaerobic metal-reducing and sulphate-reducing bacteria including *Escherichia coli, Geobacter sulfurreducens, Geobacter metallireducens, Shewanella putrefaciens* or *Desulfovibrio desulfuricans* (Abdelouas et al., 2005; Icenhower et al., 2009; Lloyd, 2003; Lloyd et al., 2000; Wildung et al., 2000), with insoluble $^{99}Tc^{IV}$ as the final product. Technetium reduction is not necessarily caused by reducing conditions in the growth medium but is the result of a metabolic process (Henrot, 1989) whereby microbially mediated biosorption of ^{99}Tc on bacterial cells removes ^{99}Tc from solution (Abdelouas et al., 2005). Another potential biotic pathway for ^{99}Tc immobilisation involves indirect reduction of ^{99}Tc via microbially generated Fe^{2+} or sulphide (Henrot, 1989; Lloyd, 2003; Lloyd et al., 2000). Biogenic Fe^{II} has been recognised as particularly efficient in indirectly reducing ^{99}Tc (Lloyd, 2003). Whilst hematite typically sorbs ^{99}Tc rather weakly, the reactivity of Fe^{III} towards $^{99}Tc^{VII}$ can increase in the presence of specific microorganisms through bioreduction of Fe^{III} and subsequent $^{99}Tc^{VII}$ reduction (Druteikienė et al., 2014). Abiotic pathways reported in the literature include interaction with Fe-bearing soil minerals, which can increase ^{99}Tc sorption under aerobic conditions. Surface mediated reduction of Tc through interaction with abiotic Fe^{II} sorbed onto Fe-bearing minerals in soils or, to a lesser extent, by aluminosilicates has also been reported as an effective scavenging mechanism (Lloyd et al., 2000). The presence of structural Fe^{II} can enhance Tc sorption onto pyrrotine $Fe_{1-x}S$ (Shen et al., 2002), magnetite (Fe_3O_4) or wustite (FeO) (Druteikienė et al., 2014) through abiotic transfer of electrons and subsequent Tc reduction, even in the presence of oxygen.

Many of the above mechanisms have been widely reported in anaerobic environments whilst aerobic cultures of *E. coli* (Lloyd, 2003) or *Desulfovibrio sp.* (Henrot, 1989) were not found to induce changes in $^{99}TcO_4^-$ solubility or to bioaccumulate ^{99}Tc. Pertechnetate reduction requires reducing conditions which are common in waterlogged sediments or hydrogeological environments below the phreatic surface, but not frequent or persistent in agricultural soils where aerobic conditions are expected to prevail. However, it is likely that the processes described above operated to some extent in our incubation experiment. Although the microcosms were incubated under aerobic conditions and periodically aerated, the soils were biologically active and contained

decomposable organic matter with the capacity to fuel microbial activity. In the presence of moisture (soils remained moist throughout the experiment – Table 1) and soil organic matter as an electron donor, the O_2 supply can become depleted in microsites within the interstices of soil particles in which gas exchange is restricted. This may locally and intermittently induce reducing conditions as O_2 diffusion through a layer of water may be rate-limiting (Icenhower et al., 2009). In addition, local accumulation of CO_2 derived from microbial respiration may induce acidification in these microenvironments, thus enhancing abiotic sorption onto humus and other binding sites. Almost every soil is thought to contain anaerobic microsites (Van Loon, 1986). Abdelouas et al. (2005) stated that degradation of organic matter by indigenous bacteria within soil grains creates localised anaerobic conditions in otherwise aerobic soils that promote reduction and precipitation of Tc. Evidence for ^{99}Tc binding has also been reported in intermittently wet farmland soils under net oxidising conditions (Icenhower et al., 2009; Tagami and Uchida, 1996).

Of all the mechanisms suggested above, reduction via biogenic Fe^{II} seems unlikely as a dominant process in our microcosms, primarily because Fe^{II} has a stronger tendency to react with O_2 than with ^{99}Tc (Icenhower et al., 2009) and our soils were in a net aerobic state. We also observed consistent Fe_{sol} and Mn_{sol} concentrations over 900 days (Fig. S8) which indicate minimal activity of Fe^{III}-reducing microorganisms. Thus, although no redox potential measurements were taken, there was no evidence for significant changes in the electrochemical status of the 20 soils or of microbially mediated ingrowth of Fe^{2+} and Mn^{2+}. This suggests that, following exhaustion of O_2, any further reductive processes were limited to microenvironments and may not have progressed much further down the redox ladder or have been widely spread across the microcosm, whilst the bulk of the soil remained aerated. Most works in the literature have studied ^{99}Tc reduction in anoxic environments with redox potentials lying within the zone of reductive dissolution of FeOx and MnOx; very few have addressed the potential for ^{99}Tc reduction in more aerated soils. Abdelouas et al. (2005) stated that, in nitrate-rich environments such as agricultural soil, Tc^{VII} reduction was not possible and no biosorption of ^{99}Tc on cells of the denitrifying bacterium *Pseudomonas aeruginosa* occurred during nitrate reduction. However, Maset et al. (2006) observed ^{99}Tc reduction and removal from solution concurrently with nitrate reduction in

soil microcosms with 12% OC. In addition, Istok et al. (2004) found evidence for bioremoval of ^{99}Tc^{VII} in tandem with nitrate reduction from nitrate-rich groundwater in the presence of organic C. This supports the notion that (i) biologically mediated ^{99}Tc^{VII} reduction in aerated microcosms can occur via enzymatic reduction at redox potentials before the onset of Fe reduction and (ii) ^{99}Tc reduction may be kinetically restrained by the presence of labile organic matter to fuel bacterial activity. It is therefore highly likely that the longer-term decline in ^{99}Tc$_{sol}$ over time in our microcosms is associated with enzymatic reactions and microbially-mediated transformations enhancing (i) migration into organically-bound pools (^{99}Tc$_{sol}$ to ^{99}Tc$_{org}$) and direct immobilisation (^{99}Tc$_{sol}$ to ^{99}Tc$_{sink}$). Strong, highly significant correlations between soil properties and the fraction of ^{99}Tc that remains in solution after 900 days i.e. C (Fig. S5) suggest that the rates of these microbially driven reactions are enhanced by low pH and high OC. The slow rate coefficient of ^{99}Tc$_{sol}$ depletion (k_{slow} acting on fraction B in Eq. 1) would potentially be the rate limiting parameter for slow, longer term ^{99}Tc$_{sol}$ to ^{99}Tc$_{org/sink}$ transformations to occur.

Changes in ^{99}Tc$_{org}$ reflected a complex combination of gains from Tc$_{sol}$ and Tc$_{ads}$ and losses to Tc$_{sink}$ over the course of the (Fig. 1). The soluble and organically bound pools are also closely interlinked in the long term as the significant relationships between model kinetic parameters for changes in ^{99}Tc$_{sol}$ and ^{99}Tc$_{org}$ suggest (Fig. S7). Thus, greater proportions of rapidly removed ^{99}Tc$_{sol}$ (A) were associated with increased 'fast' and 'slow' rates of ^{99}Tc$_{org}$ formation (R_1 and R_2). Low residual ^{99}Tc$_{sol}$ fractions (C parameter in Eq. 1) were also indicative of greater rates of ^{99}Tc$_{org}$ formation (R_1 and R_2) in the long term (Fig. S7).

Sufficient labile organic matter and moisture favour biotic reduction of ^{99}Tc$_{sol}$^{VII} in microenvironments thus enabling (i) precipitation of sparingly soluble ^{99}TcO$_2 \cdot n$H$_2$O and/or (ii) greater ^{99}Tc^{IV} sorption onto organic matter as an intermediate step for further complexation reactions ultimately resulting in ^{99}Tc immobilisation (i.e. transfer to ^{99}Tc$_{sink}$). Stabilisation of ^{99}Tc$_{org}$ after 400 days suggests that (i) the rates of ^{99}Tc$_{sol/ads}$ to ^{99}Tc$_{org}$ transfer slowed down after 1 yr and/or (ii) active ^{99}Tc$_{sol/ads}$ to ^{99}Tc$_{org}$ transfers are counterbalanced by immobilisation processes causing ^{99}Tc$_{org}$ to ^{99}Tc$_{sink}$ transfers with the result that there is no net increase in the ^{99}Tc$_{org}$ reservoir over time. Our observations indicate that OC may accelerate the transformations

responsible for the otherwise slow migration of ^{99}Tc to more recalcitrant organic pools in soil (^{99}Tc$_{sink}$). It is also possible that the observed trend of ^{99}Tc$_{sink}$ over the course of the experiment reflects an inefficiency in the TMAH extraction of humic material. However previous studies have demonstrated organic matter can act as a sink for reduced Tc species (Ashworth and Shaw, 2005) and evidence for the formation of Tc species associated with humic substances following pertechnetate reduction has been found using spectroscopic techniques (Maes et al. 2004). Organic matter and its ability to form strong complexes play a critical role in the progressive immobilisation of ^{99}Tc. ^{99}Tc$_{org}$ to ^{99}Tc$_{sink}$ transfers would be driven by complex interactions between ^{99}Tc^{IV} following pertechnetate reduction and humic substances present in soil including metal-humate complexation and subsequent precipitation (Sekine et al. 1993), oxidic polymer colloid formation followed by interaction with humic substances (Maes et al., 2004) or formation of organic coatings on mineral surfaces (Koch-Steindl and Pröhl, 2001).

Reliability of model predictions

We used an 'offset' double exponential kinetic model to represent the time-dependent decline in soluble forms of ^{99}Tc in soils. The slow component of the kinetic system (i.e. the slow rate coefficient, k_{slow}) enabled estimation of the time required to reduce the soluble ^{99}Tc$_{sol}$ subject to slow removal (*B*) by 99% (*T$_{99}$*). This addresses the second of the two questions tackled in this study - over what experimental timescales must we measure Tc reaction kinetics in order to make reliable long-term predictions of ^{99}Tc impact in the terrestrial environment?

A major control on T$_{99}$ was found to be the size of the fraction to be removed, with lower values of *B* (Eq. 1) shortening the period required to reduce ^{99}Tc$_{sol}$ to 1% of *B*. Thus, values of *T$_{99}$* less than the period of the incubation experiment were observed in peaty, acidic and highly reactive soils where immediate fixation processes are dominant i.e. those soils with a large *A* fraction in relation to *B* and *C* (e.g. DY-G, DY-M). To a lesser extent, other near-neutral to acidic woodland and grassland soils with sufficient OC to prompt fast ^{99}Tc$_{sol/ads}$ to ^{99}Tc$_{org}$ transformations and enhance the magnitude of the *A* fraction have relatively low depletion periods of up to 3.5 yr (Fig. 5). These estimates can be considered to be reasonably reliable given that (i) model fits were very good for these soils, especially for the longer term experimental data and (ii) ^{99}Tc$_{sol}$ in

these soils was low towards the end of the experiment and appeared to be approaching the persistently soluble fraction, *C* (Fig. 3).

Depletion times shorter than the incubation experiment were also observed for poorly organic, calcareous soils (e.g. SR-A and WK-A) in which $^{99}Tc_{sol}$ also appeared to be approaching the persistently soluble fraction. High pH and low OC (i) do not enable fixation (i.e. *A*=0) and (ii) lead to poorly reactive soils with limited capacity for long term ^{99}Tc transformation and binding, with the result that ^{99}Tc removal from solution was marginal and ^{99}Tc largely remained as persistently soluble $^{99}Tc_{sol}$ over the long term (i.e. *C*≥80%, Fig. 5).

By contrast, the experimental data suggest that near neutral, moderately organic soils are far from reaching steady state with respect to soluble ^{99}Tc within the duration of the experiment. Prediction of timeframes for reduction in ^{99}Tc solubility may not be accurate for soils actively losing soluble $^{99}Tc_{sol}$ beyond the 2.5 yr incubation period, given that changing reaction rates may introduce uncertainty in the estimates. However, our findings provide solid evidence that short-term experiments (less than 1 or 2 years) may not be used reliably to predict the long-term/equilibrium solubility and immobilisation of ^{99}Tc and, potentially, other radionuclides characterised by slow sorption rates. This is of particular relevance in the context of long-term radiological risk assessments.

5. CONCLUSIONS

The removal of ^{99}Tc from solution was very slow in relation to other radionuclides and our observations suggest that steady state conditions were not attained in the majority of soils, even after 2.5 years incubation. Reduction in soluble ^{99}Tc over time followed a dual rate, double exponential kinetic model and included (i) a fast component reflecting immediate removal enhanced by low pH; (ii) a slowly removed fraction largely controlled by pH and organic matter; and (iii) a persistently soluble Tc fraction. The slowest rates of sorption were seen in calcareous

soils which clearly highlights potential risk to limestone and chalk aquifers; the rendzina soil types overlying such aquifers would clearly fail to intercept deposited ^{99}Tc. Soil polyvalent metal oxides only played a marginal role in sequestering ^{99}Tc. By contrast, a combination of high OC concentrations and low pH produced faster sorption kinetics. The ability of soil humus to form strong complexes with ^{99}Tc is key to the progressive immobilisation of ^{99}Tc in soil. Our data suggest that short-term experiments (<1–2 years) may not be used reliably to predict long-term solubility and bioaccessibility of ^{99}Tc, particularly for soils with low to moderate OC contents. Our findings are of practical significance in risk assessment calculations for facilities such as radioactive waste repositories, whether based on generic or site-specific criteria. While our experimental study has not considered the fate and behaviour of ^{99}Tc in every possible soil type, the range of physico-chemical characteristics examined is wide enough to encompass the environmental circumstances under which many risk assessments will be made.

Author contributions

EB, GS, NC and SY conceived and planned the experiments. EB, GS, MI and SY sampled the soils and set up the incubation experiment. MI and HS carried out the sampling and analyses. MI processed the experimental data and carried out interpretation of results with help from GS and SY. GS performed the model fittings. MI took the lead in writing the manuscript but all authors discussed the results, provided critical feedback and helped shape the manuscript.

Declaration of interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

RESEARCH DATA

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FIGURE CAPTIONS

Figure 1. Changes in the concentrations of ^{99}Tc in the soluble (a), adsorbed (b), organic (c) and sink (d) pools over the course of 897 days incubation in 20 soils. Circles and whiskers denote median values and interquartile (25–75%) range for all soils within the specified land use categories, respectively. For ^{99}Tc$_{sol}$ and ^{99}Tc$_{org}$ median values, a double exponential model and a dual rate model (respectively) have been fitted.

Figure 2. Relationships between soluble Tc (^{99}Tc$_{sol}$), organic matter (OC) and soil pH. Data points are averages of 3 microcosms.

Figure 3. Kinetics of removal of ^{99}Tc$_{sol}$ from the soluble (KNO$_3$ extractable) pool in arable (a), grassland (b), woodland (c) and moorland (d) soils over the course of 897 days. The points are experimental data through which an offset double exponential model (Eq. 1) has been fitted. Soil codes and pH values are listed in Table 1.

Figure 4. Chromatograms of soluble extracts of selected microcosms (DYG, NP, TK and BHG) at early retention times (<2 minutes) showing unidentified ^{99}Tc$_{sol}$ species.

Figure 5. Total time (T_{99}) required to deplete the initially soluble ^{99}Tc$_{sol}$ fraction B by 99%, ^{99}Tc$_{sol}$ fractions subject to fast (A) and slow (B) removal and persistently soluble ^{99}Tc$_{sol}$ remaining after the experiment (C). The dotted line denotes the timeframe for the incubation experiment.

Figure 6. Relationships between soil pH, organic C (OC) and the concentrations of ^{99}Tc in the adsorbed (a), organic (b) and sink (c) pools at 143 days (+), 431 days ($\triangle$) and 897 (O) days incubation. Data points are averages of 3 replicated microcosms for each soil.
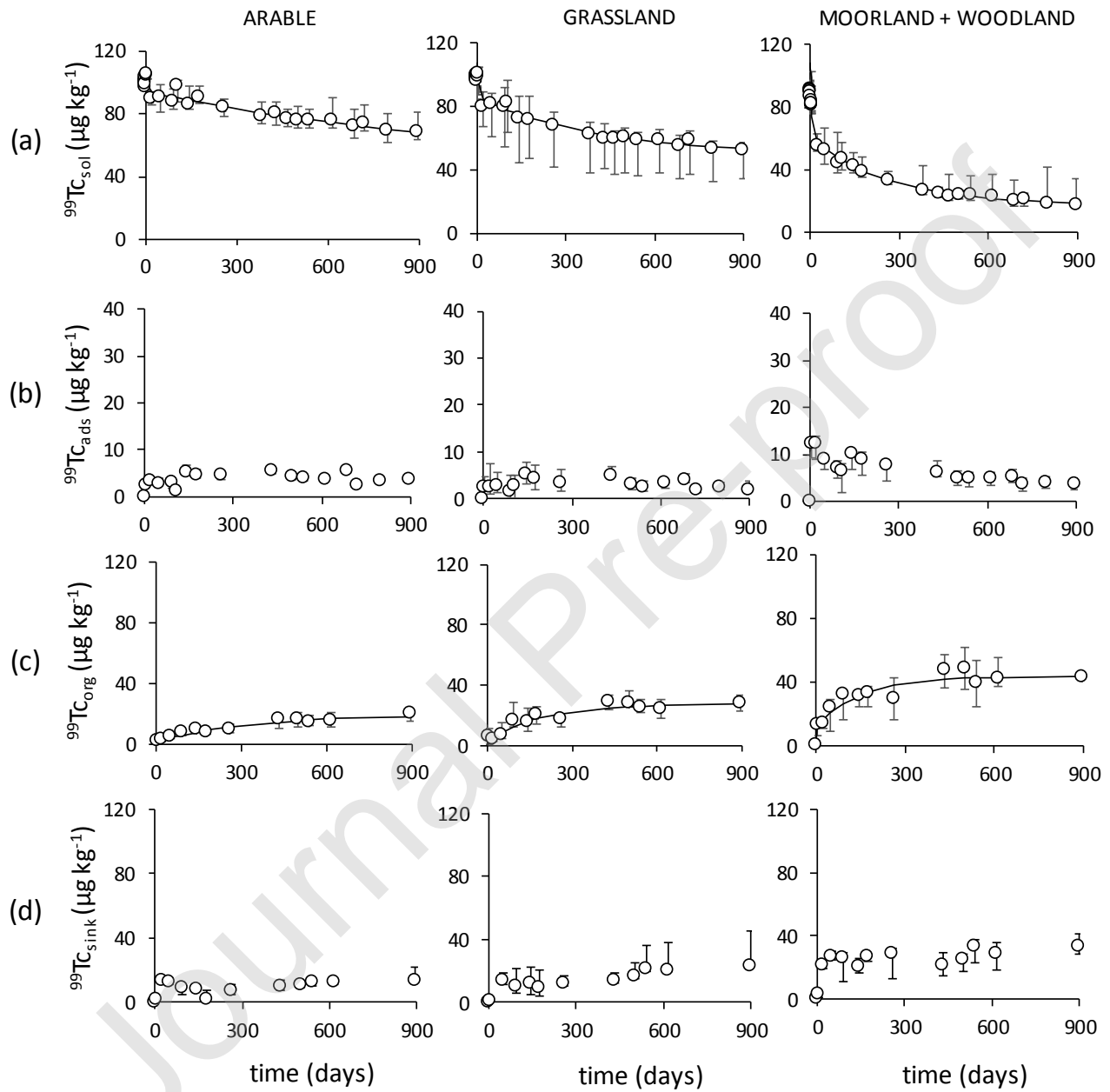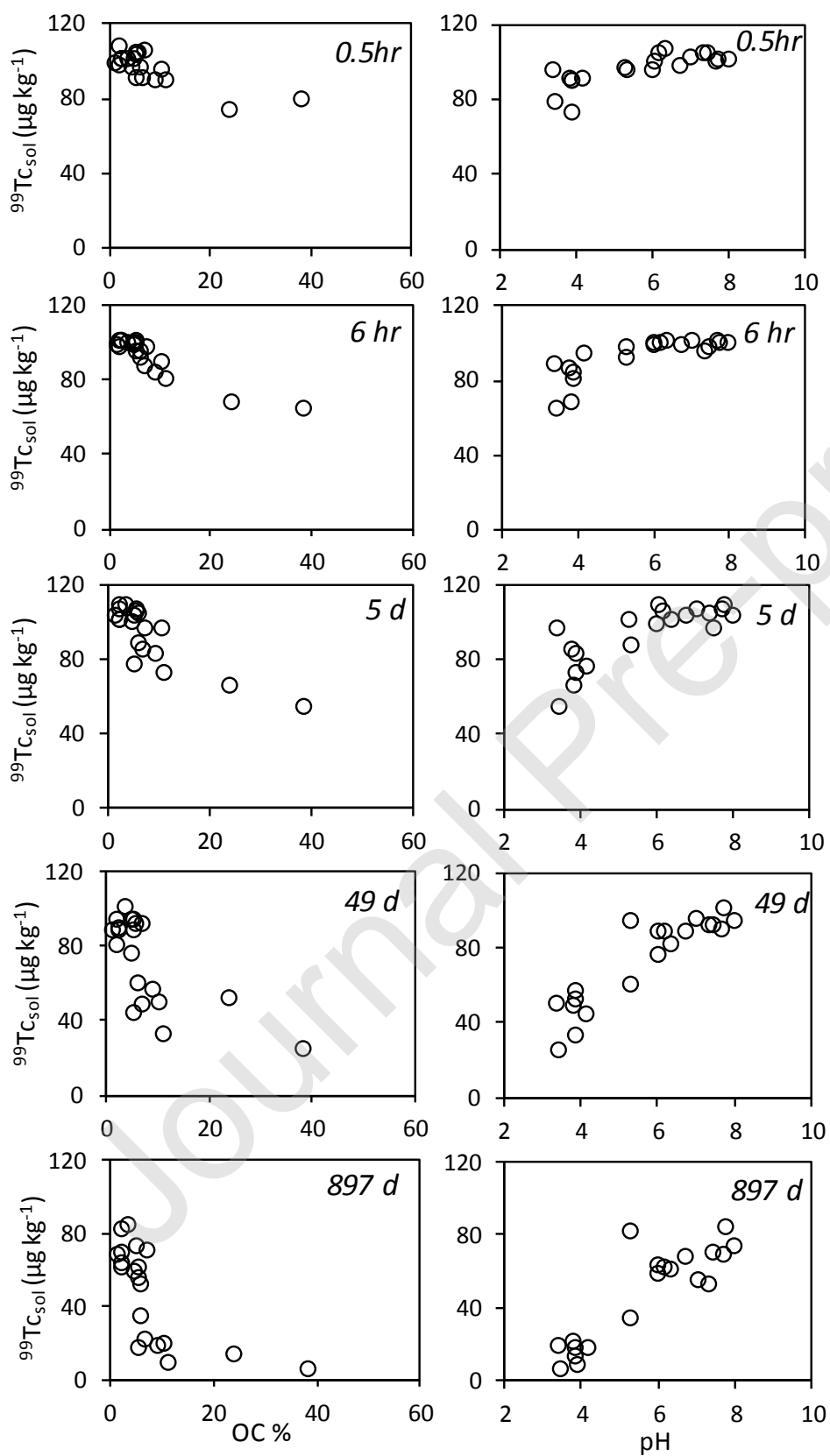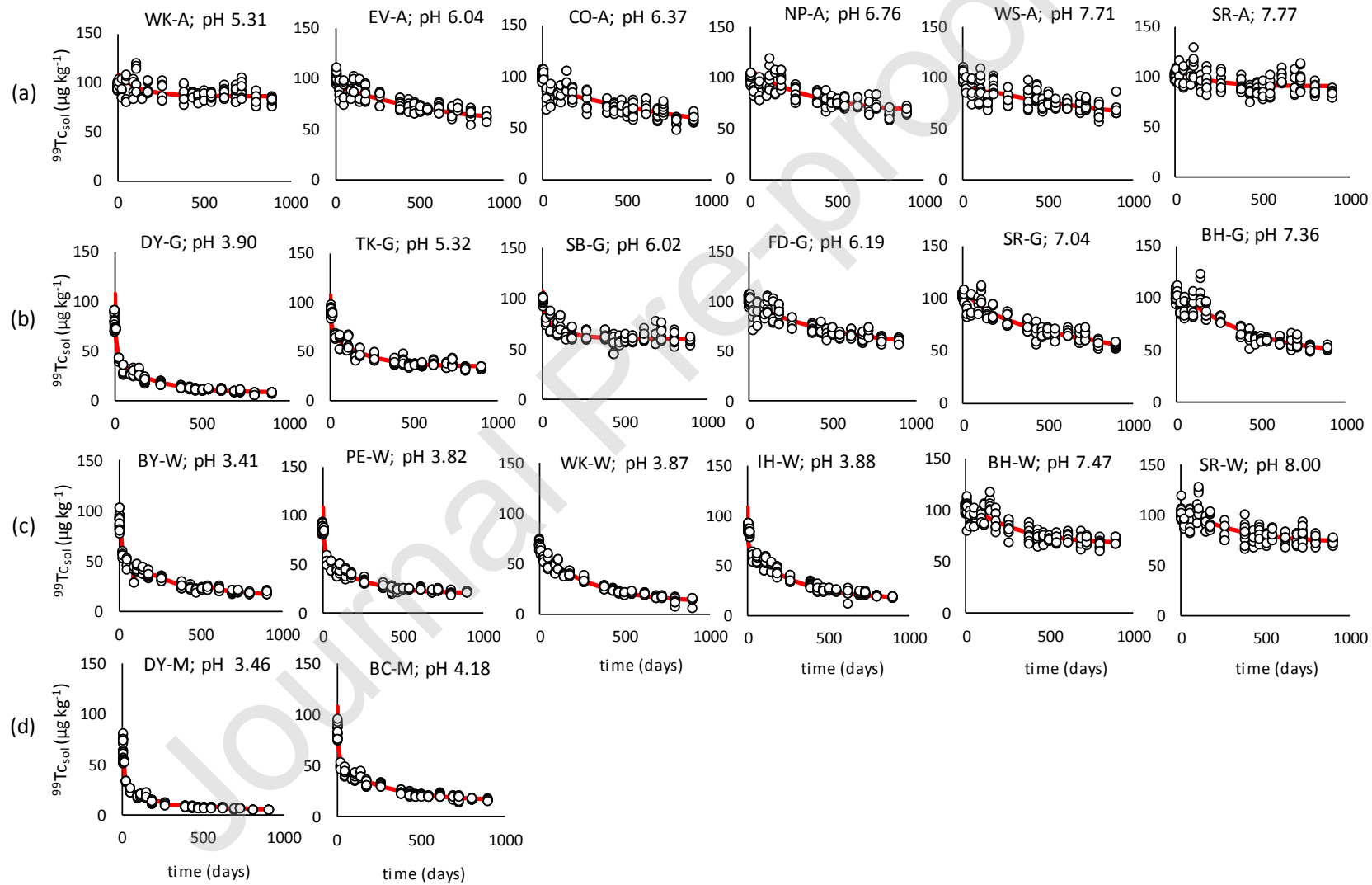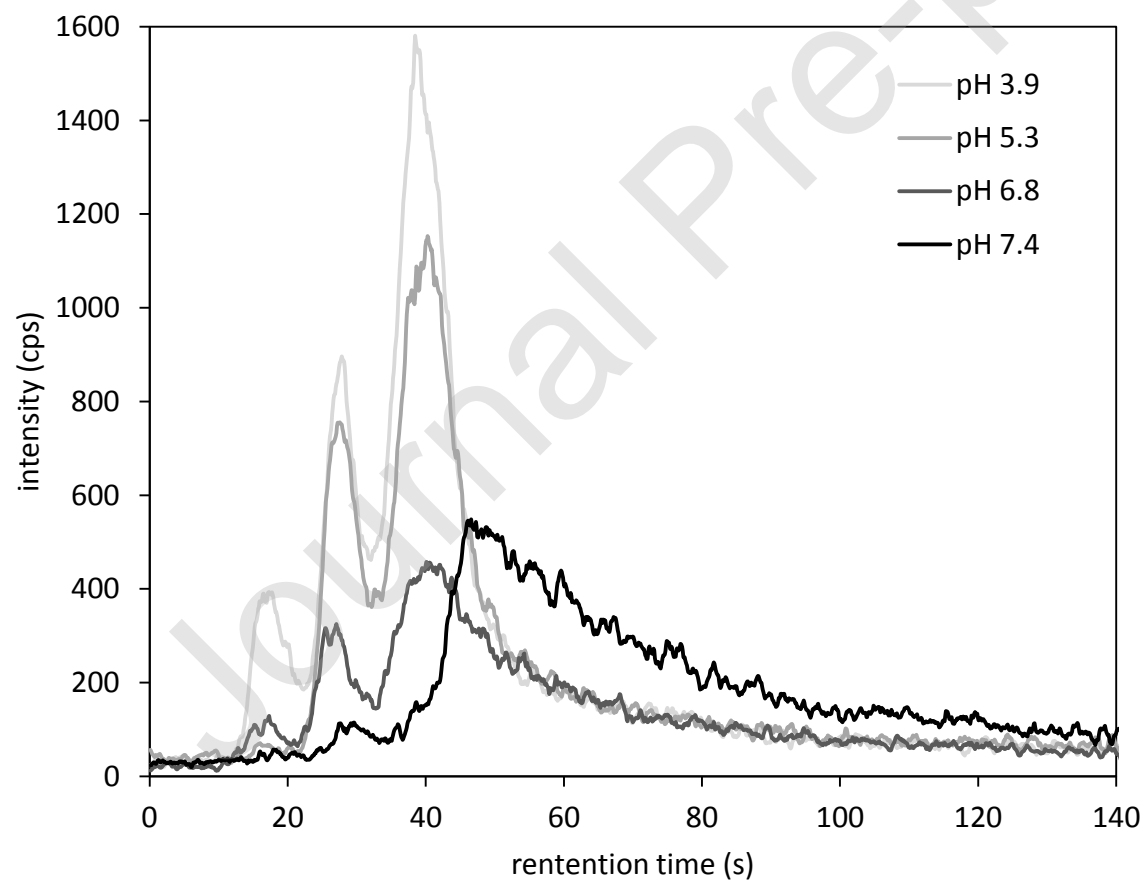
Figure 1

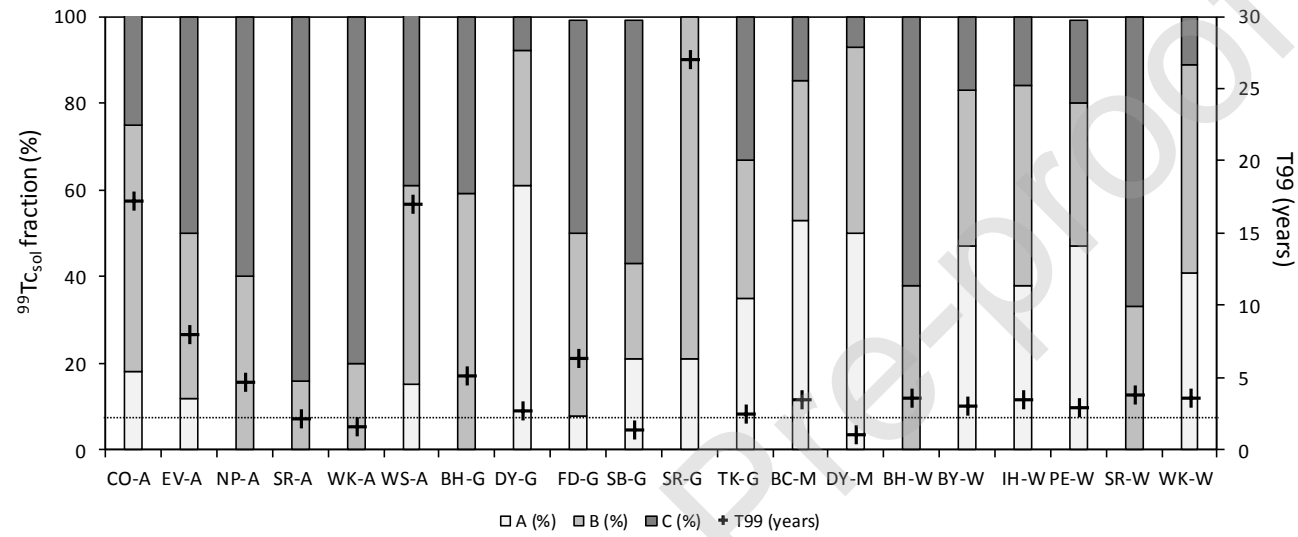**Figure 2**

Figure 3

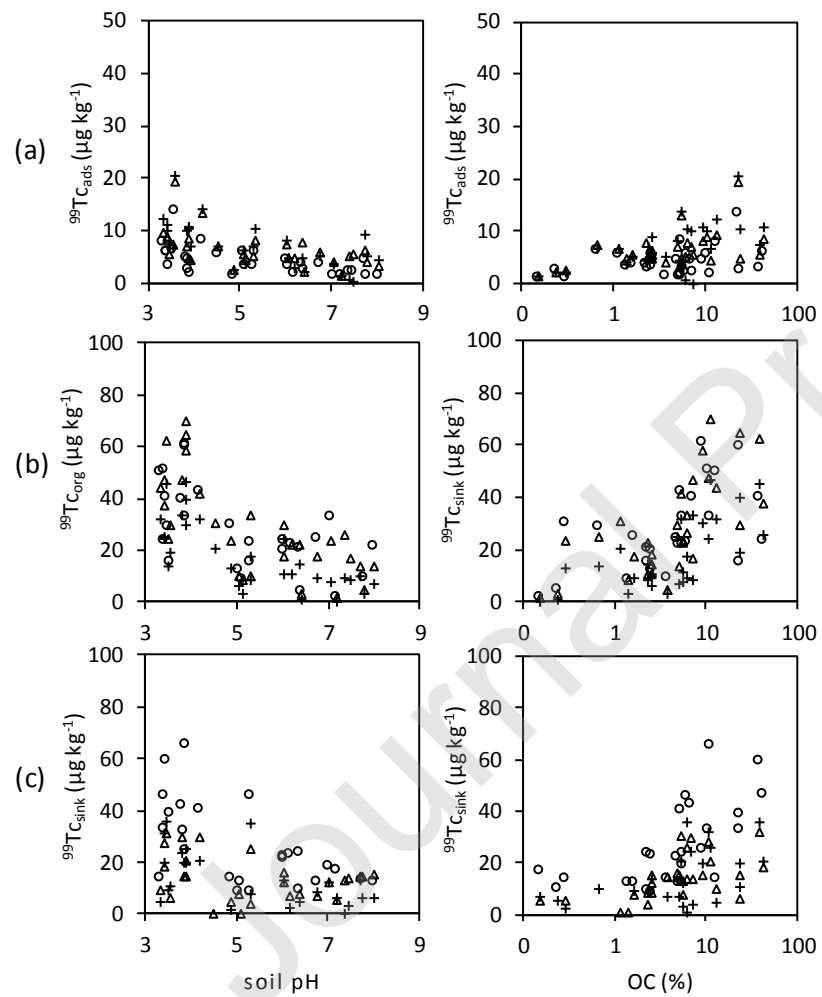**Figure 4**

Figure 5

Figure 6

Table 1. Location and general properties of the soils in this study, listed in order of land use. Bdl denotes below the detection limit.

code	land use	Latitude	Longitude	% inorg C	% organic C	pH	total concentrations mg kg⁻¹ Al	Mn	Fe	Free amorphous oxides mg kg⁻¹ Al	Mn	Fe	Total free oxides mg kg⁻¹ Al	Mn	Fe	incubation moisture content Table 3% wt
CO-A	arable	52° 49' 36.9" N	1° 13' 35.08" W	Bdl	2.3	6.37	26707	508	20965	633	317	3386	751	356	9372	9
EV-A	arable	52° 50' 39.43" N	1° 11' 25.83" W	0.043	2.6	6.04	43275	934	34961	1244	622	4233	1245	736	14217	12
NP-A	arable	52° 51' 38.39" N	1° 7' 30.47" W	Bdl	1.7	6.76	15873	501	17725	637	277	2103	617	331	7531	9
SR-A	arable	52° 51' 3.19" N	0°40'35.01"W	5.33	3.8	7.77	23207	682	22515	1333	232	1181	1176	364	12425	9
WK-A	arable	52° 49' 47.96" N	1° 14' 24.12" W	Bdl	2.4	5.31	19815	645	29614	762	404	3688	842	414	9270	13
WS-A	arable	52° 51' 9.31" N	1° 7' 36.4" W	0.74	2.6	7.71	42149	1037	33255	604	349	1205	456	431	7166	14
BH-G	grassland	52° 48'24.77"N	1°23'58.86"W	1.16	6.2	7.36	27237	4451	30438	1487	3143	5184	1110	3525	14599	20
DY-G	grassland	53° 18'55.30"N	1° 36'1.37"W	Bdl	11.4	3.90	15841	43	6925	863	18	2264	1089	36	5563	31
FD-G	grassland	52° 49' 54.13" N	1° 13' 35.92" W	Bdl	5.7	6.19	57058	1053	52789	1626	505	8148	1130	679	18387	24
SB-G	grassland	52° 47' 23.53" N	1° 27' 58.07" W	Bdl	5.0	6.02	22103	460	13775	1181	289	5436	1294	331	10073	15
SR-G	grassland	52° 51' 0.83" N	0° 40' 39.93"W	0.38	5.7	7.04	36862	874	50808	1985	529	3893	1956	666	22668	22
TK-G	grassland	52° 47' 36.62" N	1° 28' 29.94" W	Bdl	6.3	5.32	40942	303	25256	2041	160	7069	1904	165	11484	20
BC-M	moorland	53° 12'44.29"N	1° 5'33.07"W	bdl	5.5	4.18	21124	77	16124	876	6	4841	995	22	7850	15
DY-M	moorland	53° 18'42.34"N	1° 35'59.93"W	Bdl	38.6	3.46	10439	43	5759	2430	18	3421	2987	24	3940	36
BH-W	woodland	52° 48'23.80"N	1°24'5.18"W	2.83	7.5	7.47	23500	2724	25395	880	1398	3126	675	1535	10514	16
BY-W	woodland	52° 49' 42.66" N	1° 27' 51.02" W	Bdl	10.6	3.41	30226	141	22966	1347	55	6978	1634	90	14285	21
IH-W	woodland	52° 44' 54.74" N	1° 17' 51.89" W	Bdl	9.5	3.88	27554	185	18013	1604	60	4178	1826	95	9496	20
PE-W	woodland	53° 12'44.41"N	1° 5'53.23"W	Bdl	7.1	3.82	18022	91	7655	670	38	1806	756	55	4720	12
SR-W	woodland	52° 50' 58.28" N	0°40' 33.61"W	3.75	5.2	8.00	28029	694	25431	1813	321	1650	-	-	-	13
WK-W	woodland	52° 49' 51.48" N	1° 14' 17.8" W	Bdl	24.4	3.87	11025	233	13202	1365	143	3578	1444	198	5778	37

Table 2. Sequential extraction scheme used to fractionate ^{99}Tc incubated in the soil microcosms. The extracted concentrations are reported in μg ^{99}Tc kg^{-1} DW.

Symbol	Description	Extractant	Comments
^{99}Tc$_{sol}$	Soluble ^{99}Tc freely extractable from the soil solution	0.01 M KNO$_3$	Extractant approximates the ionic strength of soil pore water
^{99}Tc$_{ads}$	^{99}Tc specifically adsorbed to Al and Fe oxides	0.16 M KH$_2$PO$_4$	Phosphate is a powerful competitor for anions adsorbed on Fe/Al/Mn oxides
^{99}Tc$_{org}$	^{99}Tc associated with alkaline-extractable organic matter	10% tetra methyl ammonium hydroxide (TMAH)	The high pH of TMAH mobilizes humic and fulvic acids
^{99}Tc$_{sink}$	Residual ^{99}Tc not extractable	-	Total ^{99}Tc added minus the sum of extractable ^{99}Tc
^{99}TcO$_4$$^-$$_{sol}$	Pertechnetate	0.01 M KNO$_3$	Ion chromatography linked to ICP-MS
^{99}TcO$_4$$^-$$_{ads}$	Pertechnetate	0.16 M KH$_2$PO$_4$	Ion chromatography linked to ICP-MS

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Table 3. Correlation analysis between modelled kinetic parameters for $^{99}Tc_{sol}$ and $^{99}Tc_{org}$ and soil properties.

Correlating Parameters	R^2 (p)	Direction	Regression equation
A% vs pH	0.71 (<0.001)	-	$\log(A) = 2.255 - 0.1573\ pH$
A% vs OC%	0.44 (0.009)	+	$\log(A) = 1.014 + 0.5217\ \log(OC)$
A% vs C%	0.69 (<0.001)	-	$\log(A) = 2.483 - 0.7641\ \log(C)$
R_1 vs *A*%	0.42 (0.031)	+	$\log(R_1) = -0.1022 + 0.9058\ \log(A)$
R_2 vs *A*%	0.34 (0.030)	+	$\log(R_2) = -1.742 + 0.6711\ \log(A)$
C% vs pH	0.69 (<0.001)	+	$\log(C) = 0.5061 + 0.1736\ pH$
C% vs OC(%)	0.56 (<0.001)	-	$\log(C) = 2.053 - 0.7402\ \log(OC)$
C% vs R_1	0.47 (0.007)	-	$\log(C) = 2.185 - 0.6289\ \log(R_1)$
C% vs R_2	0.62 (<0.001)	-	$\log(C) = 0.8419 - 0.6997\ \log(R_2)$
k_1 vs pH	0.34 (0.029)	+	$\log(k_1) = -0.1800 + 0.1224\ pH$
k_2 vs pH	0.23 (0.034)	-	$\log(k_2) = -1.866 - 0.08550\ pH$
R_1 vs OC%	0.292 (0.046)	+	-
k_{slow} vs pH	0.20 (0.046)	-	$\mathrm{Log}(k_{slow}) = -1.936 - 0.1014\ pH$
k_{slow} vs OC%	0.18 (0.060)	+	$\mathrm{Log}(k_{slow}) = -2.868 + 0.4607\ \log(OC)$
B% vs T_{99} (yr)	0.59 (<0.001)	+	$T_{99} = -0.8.045 + 0.356\ B$

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