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Uranium diffusion and time-dependent adsorption–desorption in soil: a model and experimental testing of the model

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Running title: Uranium diffusion

Summary

Most past research on uranium (U) transport and reaction in the environment has been concerned with groundwater contamination, and not with uptake by plants or soil biota, both of which operate over much smaller time and distance scales. We developed and tested a model of U diffusion and reaction in soil at scales appropriate for uptake by plant roots, based on a model we developed in an earlier paper. The model allows for the speciation of U with hydroxyl, carbonate and organic ligands in the soil solution, and the nature and kinetics of sorption reactions with the soil solid. The model predictions were compared with experimentally-measured concentration-distance profiles of U in soil adjusted to different pHs and CO_2 pressures. Excellent agreement between observed and predicted profiles was obtained using model input parameters measured or otherwise estimated independently of the concentration-distance profiles, showing that the model was a correct description of the system and all important processes were allowed for. The importance of the kinetics of U adsorption and desorption on the time-scale of diffusion through the soil is highlighted. The results are discussed in terms of the uptake of U by plant root systems, as modelled in the earlier paper.

Highlights

- We developed a model of U diffusion and reaction in soil on scales relevant to uptake by plant roots.
- We tested the model against measured diffusion profiles and obtained excellent agreement.
- The kinetics of U adsorption–desorption reactions are important.
- Reaction kinetics measured in shaken suspensions or flow-through systems are likely to be misleading.

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Introduction

Soil contamination with uranium (U) occurs from geological deposits, metal mining, nuclear waste and depleted U in weapons, and it enters the food chain largely with uptake by plants from soil. Understanding the mechanisms of plant uptake is difficult because of the complex biogeochemistry of U in soil and the involvement of complex root–soil interactions (Mitchell *et al*., 2013). Simple empirical models exist, based on soil–plant transfer functions, but are only useful for the conditions in which they have been calibrated. Most mechanistic modelling of U in the environment has been concerned with groundwater contamination, and therefore with (a) much larger scales than for root uptake and (b) mass flow-dominated transport, whereas U uptake by roots is generally diffusion-limited (next paragraph). In an earlier paper (Boghi *et al*., 2018) we developed a model of U uptake by plants allowing for transport through soil to root surfaces, root-induced changes in the soil affecting U mobility and rates of transport across the root–soil boundary. We compared the model's predictions with published information on uptake rates under different soil conditions, but did not test it rigorously against experiments. In this paper we provide such a rigorous testing.

Simple calculations show that rates of uptake are typically far greater than can be explained by mass flow alone, given typical U concentrations in soil solutions and water inflow into roots. Table S1 (Supporting Information) gives such calculations for U uptake by ryegrass (*Lolium perenne* L) in a range of soils, based on data of Duquène *et al*. (2010). This suggests that uptake is limited by diffusion through the soil, and therefore that transport across the soil–root boundary is sufficiently fast that a depletion zone develops around the root, through which U diffuses. Uranium uptake is enhanced where roots are colonized by mycorrhizal fungi, although root–shoot translocation is then often impeded (Davies *et al*., 2015). Uptake into mycorrhiza must also be limited by diffusion through the soil.

Uranium is present in soil solutions and is taken up from these by roots as the uranyl (UO_2^{2+}) cation and as complexes with carbonate (CO_3^{2-}) and organic (L^-) ligands (Figure 1). The complexes are differentially sorbed on soil surfaces, and the extent of sorption as well as the proportions of the different complexes in solution are functions of pH and CO_2 pressure, such that the sorption–pH relation is bell-shaped with a peak around neutral pH but shifting to lower pH with increasing CO_2 pressure (Davis *et al*., 2004; Geckeis *et al*., 2013; Mitchell *et al*., 2013). Therefore, diffusion through the soil solution to absorbing roots might be sensitive to the changes in rhizosphere pH and CO_2 pressure that are commonly caused by roots. Further, the interchange of U between the soil solid and solution may be rate-limiting. Experiments on sorption kinetics in soils and sediments generally show desorption of U is initially fast, but then continues at a much slower rate for some weeks (Braithwaite *et al*., 1997; Qafoku *et al*., 2005; Handley-Sidhu *et al*., 2009; Stoliker *et al*., 2013). The model of Boghi *et al*. (2018) predicts that such time-dependency should be important on

the time-scale of U uptake by plant roots. The rate-limiting step is likely to be slow access to or from sorption sites within soil aggregates by diffusion in the intra-aggregate pore space, rather than slow chemical reactions as such (Nye & Staunton, 1994; Ptashnyk *et al*., 2010). However the available data on sorption kinetics is mainly from shaken suspension experiments in which sorption is accelerated by convection and disaggregation of the soil, or from breakthrough curves in flow-through systems, in which sorption is also accelerated by convection (Qafoku *et al*., 2005; Stoliker *et al*., 2013).

In this paper we test Boghi *et al*.'s (2018) model against experimentally measured rates of U diffusion through soil under different pHs and CO_2 pressures. We measured the diffusion of U between two half-cells of soil, one of which initially contained U and the other not. From the concentration-distance profiles we gauged rates of desorption in the source cell and adsorption in the sink cell. We made experiments in soils adjusted to different pHs and CO_2 pressures in the ranges in which U mobility is expected to be large. We compared the measured profiles with the predictions of Boghi *et al*.'s (2018) model, reformulated for the planar geometry and boundary conditions of the experiments. We also measured the diffusion of non-adsorbed Br^- ions in our half-cell experimental system to determine the soil diffusion coefficient in the absence of sorption and to confirm that the system behaved as expected from theory.

Theory

Uranium diffusion and reaction

In our experimental system, two half-cells of soil are placed in contact, one containing U and the other not, and the cells are incubated so that U diffuses from the U-containing cell to the other. After suitable intervals, concentration-distance profiles through the soil are determined. The continuity equation for diffusion and reaction is:

$$\frac{\partial C}{\partial t} = \frac{\partial}{\partial x}\left(D \frac{\partial C}{\partial x} \right), \tag{1}$$

where C is the concentration of U in the whole soil and D is its diffusion coefficient in the soil, given by

$$D = D_{\mathrm{L}} \theta f \frac{\mathrm{d}C_{\mathrm{L}}}{\mathrm{d}C} \tag{2}$$

where D_{L} is the diffusion coefficient in free solution, θ is the soil volumetric moisture content, f is an impedance factor and C_{L} is the concentration of U species (free and complexed) in the soil solution. The boundary conditions are

$$\begin{aligned} C = C_1 \quad & x < 0 \quad & C = C_0 \quad & x > 0 \quad & t = 0, \\ C = C_1 \quad & x = -\infty \quad & C = C_0 \quad & x = \infty \quad & t \geq 0, \end{aligned} \tag{3}$$

where C_1 is the concentration in the source cell, C_0 is the concentration in the sink cell (= 0), $x = 0$ is the inter-cell boundary and $x = \infty$ is the semi-infinite far-field boundary.

Boghi *et al*. (2018) define two types of U in the soil solid consistent with past work on sorption kinetics (references in Introduction): one that exchanges effectively instantaneously with U species in the soil solution and one that exchanges more slowly. Hence

$$C = \theta C_{\mathrm{L}} + \rho\left(C_{\mathrm{S1}} + C_{\mathrm{S2}}\right), \tag{4}$$

where C_{S1} and C_{S2} are the concentrations of fast- and slow-reacting U (per unit whole soil mass) and ρ is the soil bulk density. Therefore,

$$\frac{\partial C}{\partial t} = \theta \frac{\partial C_{\mathrm{L}}}{\partial t} + \rho\left(\frac{\partial C_{\mathrm{S1}}}{\partial t} + \frac{\partial C_{\mathrm{S2}}}{\partial t}\right). \tag{5}$$

For the fast-reacting U,

$$\frac{\partial C_{\mathrm{S1}}}{\partial t} = \frac{\partial C_{\mathrm{S1}}}{\partial C_{\mathrm{L}}}\frac{\partial C_{\mathrm{L}}}{\partial t} = b\frac{\partial C_{\mathrm{L}}}{\partial t}, \tag{6}$$

where the derivative b is the buffer power for the solid–solution distribution of fast-reacting U, which is a function of pH and CO_2 pressure (Boghi *et al*., 2018, Equations 1–7; next section). For the slowly-reacting U, we assume reversible first-order kinetics (Boghi *et al*., 2018, Equation 8):

$$\frac{\mathrm{d}C_{\mathrm{S2}}}{\mathrm{d}t} = k_1 C_{\mathrm{S1}} - k_2 C_{\mathrm{S2}}, \tag{7}$$

where k_1 and k_2 are forward and backward rate constants. In Equation (1),

$$D\frac{\partial C}{\partial x} = D\frac{\partial C}{\partial C_{\mathrm{L}}}\frac{\partial C_{\mathrm{L}}}{\partial x} = D_{\mathrm{L}}\theta f\frac{\partial C_{\mathrm{L}}}{\partial x}. \tag{8}$$

Combining Equation (1) with Equations (5)–(8) and rearranging gives

$$\left(\theta + \rho b\right)\frac{\partial C_{\mathrm{L}}}{\partial t} = \frac{\partial}{\partial x}\left(D_{\mathrm{L}}\theta f\frac{\partial C_{\mathrm{L}}}{\partial x}\right) - \rho\left(k_1 C_{\mathrm{S1}} - k_2 C_{\mathrm{S2}}\right). \tag{9}$$

Equations for U speciation and fast sorption. In our experimental system, the soil contains Ca^{2+}, H^+, H_2CO_3, HCO_3^-, CO_3^{2-}, Cl^- and L^- (representing organic ligands) in the soil solution and Ca^{2+} in the soil exchange complex, in addition to U. Over the range of pH, P_{CO_2} and dissolved U concentration in our experiments, the important U species in solution are UO_2^{2+}, UO_2CO_3,

$Ca_2UO_2(CO_3)_3$ and $CaUO_2(CO_3)_3^{2-}$ (Figure S1, Supporting Information, gives speciation calculations) and to a lesser extent UO_2L^+; the solution is under-saturated with respect to known U minerals. The total concentration of U species in the soil solution is therefore:

$$C_L = [UO_2^{2+}]_L + [UO_2CO_3]_L + [Ca_2UO_2(CO_3)_3]_L + [CaUO_2(CO_3)_3^{2-}]_L + [UO_2L^+]_L = [UO_2^{2+}]_L \left\{ \begin{array}{r} 1 + K_{UO_2CO_3}[CO_3^{2-}]_L + K_{Ca_2UO_2(CO_3)_3}[Ca^{2+}]_L^{\,2}[CO_3^{2-}]_L^{\,3} + \\ K_{CaUO_2(CO_3)_3^{2-}}[Ca^{2+}]_L[CO_3^{2-}]_L^{\,3} + K_{UO_2L^+}[L^-]_L \end{array} \right\}, \quad (10)$$

where the *K* terms are the respective conditional equilibrium constants adjusted for activity coefficients.

The unknowns in Equation (10) are $[UO_2^{2+}]_L$, $[CO_3^{2-}]_L$ and $[Ca^{2+}]_L$. The $[CO_3^{2-}]_L$ is defined by the pH and CO_2 pressure, and $[Ca^{2+}]_L$ is defined by the electrical neutrality condition:

$$2[Ca^{2+}]_L + 2[UO_2^{2+}]_L + [UO_2L^+]_L + [H^+]_L = [Cl^-]_L + [HCO_3^-]_L + [L^-]_L + 2[CaUO_2(CO_3)_3^{2-}]_L \quad (11)$$

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We assume the concentration of the balancing anion Cl^- is constant, it being far greater than the concentrations of other anions, and that the pH is constant, which is justified by the results of Boghi *et al*. (2018) who showed that acid–base changes in U sorption reactions have a negligible effect on the soil pH.

For the fast sorption reactions, Boghi *et al*. (2018) used the generalized surface complexation model of Davis *et al*. (2004) which gives semi-empirical equations for U sorption on soils and sediments. From a sensitivity analysis of Davis *et al*.'s equations, the generally-observed dependence of U sorption on soil pH and CO_2 pressure over the relevant ranges in our experiments was best described with the following two reactions:

$$Soil–(OH)_2 + UO_2^{2+} = Soil–O_2UO_2 + 2H^+, \quad (12)$$

$$Soil–(OH)_2 + CaUO_2(CO_3)_3^{2-} = Soil–CaUO_2(CO_3)_3 + 2OH^- \quad (13)$$

and the corresponding two mass-action equilibrium equations:

$$\frac{C_{S11}[H^+]_L^{\,2}}{X_{S1}[UO_2^{2+}]_L} = K_{S,UO_2^{2+}}, \quad (14)$$

$$\frac{C_{S12}[OH^-]_L^{\,2}}{X_{S1}[CaUO_2(CO_3)_3^{2-}]_L} = K_{S,CaUO_2(CO_3)_3^{2-}}, \quad (15)$$

where $C_{S11} = [Soil–O_2UO_2]_S$, $C_{S12} = [Soil–CaUO_2(CO_3)_3]_S$, $X_{S1} = [Soil–(OH)_2]_S$, the K_Ss are conditional equilibrium constants and

$$C_{S11} + C_{S12} + X_{S1} = C_{S1} + X_{S1} = S1 \quad (16)$$

in which S1 is a constant. Therefore, for a given soil pH and CO_2 pressure and total fast-reacting U concentration, we have five unknowns: C_L, $[UO_2^{2+}]_L$, $[CaUO_2(CO_3)_3^{2-}]_L$, C_{S1} and X_{S1}. These are found with Equations (4), (10) and (14)–(16). This defines the buffer power b in Equation (6).

Solution of the equations. We solved Equation (9) subject to the initial and boundary conditions and the other equations using the Crank–Nicolson finite-difference method. Copies of the program, written in FORTRAN, are available (Supporting Information). The total soil U concentration and the values of pH, CO_2 pressure, $[Cl^-]_L$, $[L^-]_L$, ρ and θ are known from the experimental set up. The value of f is obtained from Br^- diffusion as below, and S1 is estimated from values of Davis *et al*. (2004). The following parameters were fitted to the data: $K_{S,UO_2^{2+}}$, $K_{S,CaUO_2(CO_3)_3^{2-}}$, k_1 and k_2. The fitting was done using the fmincon function in MATLAB's Optimization Toolbox to optimize agreement between the measured and predicted concentration-distance profiles. A unique set of parameters for the whole dataset was found through a fitting algorithm, which minimizes the average of the fitting errors calculated for the individual replicate runs. We assessed the global error as

$$E = \frac{1}{N}\sum_{i=1}^{N}\left|C_i^{\text{measured}} - C_i^{\text{modelled}}\right|$$

for the N experimental treatments × replicates (N = 15 given the six treatments and replicates analysed, Figures S3–S5, Supporting Information).

Bromide diffusion

We measured the diffusion of Br^- ions in our experimental system to confirm that the system behaves as expected from theory. Because Br^- ions are not adsorbed on the soil solid, the diffusion coefficient in the soil is constant and only influenced by tortuosity of the pore spacetherefore the complications of concentration- and time-dependency are avoided. Consequently the solution of the diffusion equation (Equation 1) subject to the boundary conditions in the half-cell system (Equation 3) has the simple form (Crank, 1975, Equation 2.14)

$$\frac{C - C_0}{C_1 - C_0} = \frac{1}{2}\operatorname{erfc}\left(-\frac{x}{2\sqrt{Dt}}\right), \quad (17)$$

where C is the whole-soil concentration of Br^-, subscripts 0 and 1 refer to the initial sink and source cells, respectively, erfc is the complimentary error function. For a non-adsorbed solute, $C = \theta C_L$ and in Equation (2) $\theta\, dC_L/dC = 1$ and $D = D_L f$.

Diffusion impedance factor

We measured the diffusion impedance factor, *f*, under the conditions of the main experiments by the method of Pinner & Nye (1982). A trace amount of a Br^- was deposited instantaneously on one end of a column of soil prepared as for the main experiments, and the concentration-distance profile measured (details below). The boundary conditions are

$$\begin{array}{lllll} C = C_1 & x = 0 & C = C_0 & x > 0 & t = 0 \\ C = C_0 & x = \infty & & & t \geq 0 \end{array} \qquad (18)$$

where $x = 0$ is the source boundary and $x = \infty$ is the semi-infinite far-field boundary, and the solution of Equation (1) subject to these conditions is (after Crank, 1975, Equation 2.7)

$$\frac{C - C_0}{C_1 - C_0} = \exp\left(-\frac{x^2}{4Dt}\right). \qquad (19)$$

i.e.
$$\ln\left(C - C_0\right) = \ln\left(C_1 - C_0\right) + \exp\left(-\frac{x^2}{4Dt}\right) \qquad (20)$$

Since $D = D_L f$ (last section), a graph of $\ln(C - C_0)$ against $x^2/4D_L t$ should have slope $-1/f$.

Materials and methods

Samples of topsoil (0–2-dm depth) of a typical brown earth (Wick series) were taken from Henfaes Research Centre, Bangor University, Abergwyngregyn, Gwynedd, UK (53º14’24”N 4º01’33”W). The soil was air-dried and sieved to < 0.5 mm after discarding large plant fragments. The properties of the sieved soil were pH (in 10 mM $CaCl_2$) = 6.0, CEC (cation exchange capacity) = 1.02 $cmol_c$ kg^{-1}, organic C content = 30 g kg^{-1}, clay content = 145 g kg^{-1}, silt content = 328 g kg^{-1}. The soil was washed three times with 10 mM $CaCl_2$ at a soil to solution ratio of 1:5, discarding the supernatant after each washing, and then dried and re-sieved to < 0.5 mm.

Uranium diffusion

Quantities of soil with and without U at pH 6.0, 7.0 and 7.6 were prepared as follows. Samples of air-dry soil were mixed with 150 mg kg^{-1} of ^{235}U-depleted uranium as uranyl nitrate (TAAB Laboratories Equipment Ltd, Aldermaston, UK) at a soil to solution ratio of 2:1, and allowed to equilibrate for 3 weeks. The soil was then air dried and re-sieved to < 0.5 mm. Samples of soil with and without added U were mixed with amounts of $Ca(OH)_2$ solution to adjust the soil pH (in 10 mM $CaCl_2$) to 7.0 and 7.6, and allowed to equilibrate for 3 weeks before air-drying and re-sieving to < 0.5 mm.

Pre-weighed amounts of the air-dry soil were packed into 0.29-dm internal diameter, 0.3-dm long Perspex cells to bulk density ≈ 1.4 kg dm^{-3}. To achieve uniform packing, the soil was poured into the cells in stages, tapping down with pressure applied from above. The soil was then gradually wetted from below with 10 mM $CaCl_2$ so that entrapped air was displaced, and it was then placed on a pressure plate for 10 days at 55 kPa to bring the moisture content to $\theta \approx 0.35$. Preliminary tests in which the soil was sectioned and the section weights and moisture contents determined showed that this method produced uniform bulk densities and moisture contents to within 1 standard deviation of the means. Two half-cells of soil were prepared, one with U and one without, with the same pH in both cells (either pH 6.0, 7.0 or 7.6). The cells were joined and held together with tape to ensure good inter-cell contact. They were then incubated at 20 ºC in 16-L perspex boxes containing a moisture-saturated atmosphere with either ambient or elevated P_{CO_2} maintained by passing a stream of 5% CO_2 in air through the box at 0.05 L $minute^{-1}$. The P_{CO_2} in the soil air was measured in cells incubated in this way (next section). The values were P_{CO_2} = 1.3 ± 0.1 and 6.5 ± 0.1 kPa in the ambient and elevated CO_2 treatments, respectively, and approximately constant along the length of the cells. Three replicate runs were made for each pH and P_{CO_2} combination.

After 12 days, the cells were separated, frozen in liquid nitrogen and sectioned at approximately 0.5-mm intervals parallel to the inter-cell boundary using a microtome (Griffin and George DIEH 600-B) and a stainless steel blade. A total of approx. 0.1 dm of each cell was sectioned. The thicknesses of the sections were calculated from their weights and the soil bulk density. The sections were dried at 105 °C for 24 hours and then U extracted by placing them in 8 mL of aqua regia (3:1 concentrated HCl:HNO_3) in a closed vessel overnight, and then digesting in a microwave digester (Anton Paar Multiwave 3000). The digests were filtered (Whatman 542 filters), made up to 100 mL with ultra-pure water, and stored at 4°C until their U contents were analysed by inductively coupled plasma mass spectroscopy (ICP–MS) as follows.

Samples were diluted with 0.3% aqua regia (Aristar grade) at 1:10 to reduce matrix effects, and analysed using an Agilent 7500ce ICP–MS (Santa Clara, CA, USA), with rf forward power 1540 W and reflected power 1 W, and Ar gas flows of 0.81 L $minute^{-1}$ and 0.19 L $minute^{-1}$ for carrier and makeup flows, respectively. Solutions were aspirated by a micro-mist nebuliser at a rate of 1.2 mL $minute^{-1}$. The instrument was operated in spectrum acquisition mode. Three replicate measurements were taken per sample. Standards were prepared from a single element stock solution (1000 µg U L^{-1}, PlasmaCal, SCP Science, Quebec, Canada) diluted with 0.3% aqua regia to 0.1–1000 µg U L^{-1}. An external calibration reference was prepared from Multi-Element Solution VI (Merck, Kenilworth, NJ, USA) diluted 100-fold to give 100 ug U L^{-1}. The extraction efficiency of this

method was close to 100% as measured by digesting a certified reference soil (IRMM; ERM-CC141).

CO_2 pressure in the soil air

Triplicate half-cells of soil were prepared and incubated as for the main experiments in 16 L perspex boxes containing a moisture-saturated atmosphere with either ambient or elevated P_{CO_2} maintained by passing a stream of 5% CO_2 in air through the box at 0.05 L minute^{-1}. After 48 hours, the cells were sliced axially into five sections and dissolved CO_2 in the soil solution measured as follows. Approximately 5-g subsamples of each section were placed in centrifuge filtration units (Millipore Ultrafree Centrifugal Filter Device (Burlington, MA, USA) with a 0.22-μm membrane), capped and then centrifuged at 4000 ***g*** for 15 minutes, and the soil solution collected. Dissolved CO_2 concentrations in the soil solutions were measured within a few minutes of collection using a micro-electrode (MI-720 electrode, Microelectrodes Inc, Bedford, NH, USA). Preliminary experiments showed the solution pH did not change over the few minutes between sampling and analysis, indicating no degassing of dissolved CO_2. Calibration solutions (0.25–10 % CO_2) were prepared by dissolving $NaHCO_3$ in CO_2-free ultra-pure water.

Bromide diffusion

Half-cells of soil were prepared as above, one containing Br and the other not. The Br addition was made by moistening the cell with 0.1 mM $CaBr_2$ in 10 mM $CaCl_2$ when initially wetting the soil before bringing it to the target moisture content on a pressure plate. The two half cells were joined together and incubated in a moisture-saturated atmosphere at 20 ºC for 4 hours. The cells were then sectioned as above and Br concentrations analysed by shaking the sections end-over-end for 30 minutes with 0.01 M $CaCl_2$ at 1:10 soil:solution ratio, centrifuging the resulting suspensions at 3500 ***g*** for 10 minutes, filtering (0.45 μm filters) and measuring Br in the filtrates by ICP–MS (PerkinElmer NexION 350, Boston, MA, USA). Three replicate runs were made.

Diffusion impedance factor

Cells of soil prepared as above were pulse-labelled with a trace amount of Br^- by placing a piece of cellulose acetate membrane containing 4.7×10^{-6} mol of $CaBr_2$ in 10 mM $CaCl_2$ against one end of the cell. After 5 minutes the membrane was removed, and the cell was incubated at 20 ºC for 2 hours to allow the Br pulse to diffuse into the soil. The soil was then sectioned parallel to the $x = 0$ plane and the sections analysed for Br as above. The results were plotted as $\ln C$ against $x^2/4D_L t$, and Equation (19) was fitted iteratively, progressively rejecting data far from $x = 0$ until all the remaining data agreed with the fitted values to within two standard deviations (Matschullat *et al*.,

2000). The fits to Equation (19) were made linear regression routines in SigmaPlot 11.0 (Systat Software Inc, Chicago, IL, USA).

Uranium sorption in shaken soil suspensions

Solutions of 0, 10, 12, 24, 36, 48 and 60 mg U L^{-1} in 10 mM $CaCl_2$ were made using uranyl nitrate. Aliquots (2.5 cm^3) of the solutions were added to 1 g of air-dry soils, prepared as under *Uranium diffusion*, in 12 cm^3 glass tubes. The tubes were capped with gas-tight rubber septa, and, in half of them, the headspace air was displaced with 5% CO_2 in air by passing the gas through the tubes at 1 L $minute^{-1}$ for 30 s. In preliminary tests, in which the headspace was sampled and analysed by gas chromatography, this was shown to provide a constant CO_2 pressure for the 24-hour duration of the sorption measurements. The tubes were shaken end-over-end for 24 hours at 20 °C, after which the suspension pHs were measured with a combination electrode. The suspensions were centrifuged at 3500 ***g*** for 10 minutes and filtered (0.45 μm filters), and U concentrations in the filtrates measured as above. The amounts of U sorbed were inferred from the amounts added less the amounts remaining in solution.

Results and discussion

Bromide diffusion

Figure 2a shows a plot of ln$C$ against $x^2/4D_Lt$ fora pulse application of Br^- ions on the soil in accord with Equation (19). From the slope, the diffusion impedance factor under the conditions of the main experiments was f = 0.39 (sd < 0.01, n = 2). Figure 2b shows concentration-distance profile of Br^- ions in the half-cell system used in the main experiments and corresponding predictions of Equation (17) using f = 0.39. The close agreement between the measured and theoretical profiles, independently predicted, is strong evidence that the half-cell method is sound.

Uranium diffusion

Model parameter values. The values of D_L for the U species were calculated with the Stokes–Einstein equation and the individual hydrated radii, giving for UO_2^{2+}, UO_2CO_3, $Ca_2UO_2(CO_3)_3$ and $CaUO_2(CO_3)_3^{2-}$ D_L = 7.60, 6.70, 4.60 and 5.10 × 10^{-8} dm^2 s^{-1}, respectively (these are comparable to published values of Kerisit & Liu, 2010). The values of the equilibrium constants for solution speciation were taken from MINTEQ 3.0 (Gustafsson, 2013), adjusted for ionic strength using the Davies equation. From the experimental set up, ρ = 1.4 ± 0.01 kg dm^{-3} (soil), θ = 0.35 ± 0.01, f = 0.39 (last section), $[Cl^-]_L$ = 20 mM, pH = 6.0, 7.0 or 7.6 and P_{CO_2} = 1.3 or 6.5 kPa. We set $[L^-]_L$ = 0.1 mM based on typical concentrations of metal-chelating organic anions in soil solutions of mineral soils (Jones *et al*., 2003); at the pHs and P_{CO_2} values of our experiments, the model

predictions were not sensitive to this value (Boghi *et al*., 2018). We set S1 = 5 mmol kg^{-1} based on values in Davis *et al*. (2004); this is equivalent to 50 % of the soil CEC. The addition of U to the soil was 150 mg U kg^{-1} (≡ 0.63 mmol U kg^{-1}). The following parameters were fitted to the data: $K_{S,UO_2^{2+}}$ = 2.30 × 10^{-3} mol dm^{-3} (solution), $K_{S,CaUO_2(CO_3)_3^{2-}}$ = 7.34 × 10^{19} mol dm^{-3} (solution), k_1 = 6.95 × 10^{-6} s^{-1} and k_2 = 9.39 × 10^{-7} s^{-1}.

The values of the buffer power $b = dC_{S1}/dC_L$, calculated with Equations 4, 10 and 14–16, are 6.03 × 10^4, 180 and 5 dm^3 kg^{-1} at pH 6.0, 7.0 and 7.6 and P_{CO_2} = 1.3 kPa, respectively, and 1.79 × 10^4, 129 and 3 dm^3 kg^{-1} at P_{CO_2} = 6.5 kPa, respectively (Figure 3). The buffer powers obtained in shaken soil suspensions show the same trends with pH and P_{CO_2} (Figure 4), but the values are different: $b = dC_S/dC_L = nmC_L^{n-1}$ (where *m* and *n* are Freundlich coefficients fitted to the data) = 5.74 × 10^3, 428 and 10 dm^3 kg^{-1} at pH 6.0, 7.0 and 7.6 and ambient P_{CO_2}, respectively, and 5.21 × 10^3 dm^3 kg^{-1}, 60 and 6 dm^3 kg^{-1} at P_{CO_2} = 6.5 kPa, respectively.

At equilibrium, $dC_{S2}/dt = 0$ and from Equation (7), $k_1C_{S1} = k_2C_{S2}$. Therefore, since $\rho(C_{S1} + C_{S2}) >> \theta C_L$ (equilibrium C_L = 0.06, 1.2 and 48.2 μM at pH = 6.0, 7.0 and 7.6 and P_{CO_2} = 1.3 kPa, and 0.09, 8.0 and 69.9 μM at P_{CO_2} = 6.5 kPa), the fraction of total U that is reacting slowly is $C_{S2}/(C_{S1} + C_{S2}) = 1/(1 + k_2/k_1)$ = 0.88, i.e. the majority of the U in the soil.

Concentration-distance profiles. Figure 5 shows the measured U concentration-distance profiles at the three pHs and two CO_2 pressures studied, compared with the model predictions, and Table 2 shows the amounts of U transferred between the half-cell couples, calculated from the amounts accumulated in the sink cells. Replicate profiles (Figures S3–S5, Supporting Information) agreed very well. As predicted by the model, there was little diffusion of U at pH = 6, but rates increased steeply as both the pH and P_{CO_2} increased. The 5-fold increase in P_{CO_2} between the experimental treatments caused a 2.8-fold increase in U transferred at pH 7.0 and a 1.8-fold increase at pH 7.6.

A striking finding was the discontinuity in the concentration-distance profiles at the inter-cell boundary, *x* = 0. A possible explanation is that there was poor contact between the cells, resulting in a boundary layer resistance. Crank (1975, Section 3.4) showed how such an interface resistance would be expected to produce discontinuities in concentration-distance profiles, and that the effect would increase as *Dt* decreases (Crank, 1975, Fig. 3.7). The value of *Dt* for Br^- diffusion in our experimental system (= 1.1 × 10^{-3} dm^2) was comparable to that for U diffusion at pH 7.6 (= 0.8 and 1.4 × 10^{-3} dm^2 at P_{CO_2} = 1.3 and 6.5 kPa, respectively). Therefore, the smooth profiles we obtained for Br^- diffusion (Figures 2b and S2, Supporting Information), and the close agreement of these

profiles with theory, showed that there was no interface resistance. We therefore reject this explanation.

Rather we consider the discontinuity to be due to slow equilibration of diffusing U between the soil solution and soil solid, as predicted by the model. Because there is no interface resistance, the concentrations of U in the soil solution on either side of the boundary must be equal. However, if the interchange of U between the soil solid and solution is slow compared with diffusion, the whole-soil U concentration will lag behind the soil solution concentration leading to an abrupt change between the source cell, where U is desorbing from the soil solid, and the sink cell, where it is being adsorbed.

The half-time for slow equilibration is $t_{½} = \ln 2/k_2$ = 8.5 days. Boghi *et al*. (2018) showed that slow equilibration will increasingly affect rates of U diffusion in soil for $k_2 < 10^{-6}$ s^{-1} (i.e. $t_{½} > 8$ days). Such rates are reported in the literature (Braithwaite *et al*., 1997; Qafoku *et al*., 2005; Handley-Sidhu *et al*., 2009). The published measurements are, however, mostly from shaken suspension or column leaching experiments in which sorption is artificially accelerated by convection and, in shaken suspensions, disaggregation of the soil, exposing sorption sites that are otherwise accessed only slowly by intra-aggregate diffusion (Nye & Staunton, 1994; Ptashnyk *et al*., 2010). The kinetics inferred from our experimental system, in which the soil solution is stationary, are more reliable. Further, we have measured the kinetics of both adsorption, which is what is usually measured, and desorption, which is what is needed for modelling diffusion to a sink, such as a plant root.

The extent of sorption is a function of pH and P_{CO_2} because they affect both U speciation in solution and the soil surface charge. Boghi *et al*. (2018) considered only sorption of the uranyl cation, UO_2^{2+}, by the soil solid (Equation 12). However at the high pH and CO_2 pressures of our experimental system, we also found? it is necessary to allow for sorption of the $CaUO_2(CO_3)_3^{2-}$ anion to account for our results. Otherwise, the decline in fast sorption (as represented by the buffer power *b* in Equation 9) with pH above 6.0 is too steep.

Sensitivity analysis

Figure 6 shows the sensitivity of the inter-cell flux of U to the indicated parameters as they were varied about the values used in Figure 5 with pH = 7.0. It shows that at this pH and the indicated P_{CO_2}, the flux is sensitive to $K_{S,CaUO_2(CO_3)_3^{2-}}$ but not $K_{S,UO_2^{2+}}$ because UO_2^{2+} is unimportant compared with $CaUO_2(CO_3)_3^{2-}$. It also shows that we are at the upper end of the P_{CO_2} range in which further increases have an effect. Our P_{CO_2} values are at the upper end of the range found in freely-drained

soils (Greenway *et al*., 2006). Soil P_{CO_2} varies with soil organic C content, root and microbial activities, and soil moisture status because they affect both CO_2 generation and its escape by diffusion in the soil air. Therefore, values are generally at least an order of magnitude above atmospheric P_{CO_2}. Likewise the predicted flux decreased as k_2 decreased below the standard value, but was not sensitive to increases above the standard value. Changes in k_1 at constant k_2 did not have much effect. As k_1 increased from 0.1 to 10 × the standard value, the equilibrium distribution of $U = C_{S2}/(C_{S1} + C_{S2}) = 1/(1 + k_2/k_1)$ increased from 0.43 to 0.99. However, increases in k_1 would not have much influence net adsorption, and so the flux across $x = 0$ – if $k_1 C_{S1} << k_2 C_{S2}$.

Implications for U uptake by plants

We have shown that U diffusion was slow at pH < 6 but increased steeply at pH > 6. Boghi *et al*. (2018) showed that root-induced pH changes controlled by the plant's N nutrition are likely to be important in this pH range. Ammonium (NH_4^+) fed plants tend to acidify their rhizosphere, and this would tend to diminish U uptake. Nitrate(NO_3^-)-fed plants, however, make their rhizosphere more alkaline, and this would increase U uptake. The change in pH was often as much as one unit, but was sensitive to the initial pH and CO_2 pressure (Boghi *et al*., 2018).

The importance of slow equilibration shown by our results has the obvious implication that it is important to allow for it correctly in modelling U uptake. Slow equilibration has the effect of deceasing the diffusive flux to a sink such as a plant root. An implication of this is that plants with fast growing root systems will accumulate more U over time than ones with slow growing roots. Such effects will also depend on the geometry of the root system and the proportions of fine roots and root hairs because these affect the spread of depletion profiles.

Conclusions

1. Measurements of U sorption kinetics in shaken soil suspensions were compromised by the effects of convection and disaggregation of the soil, exposing otherwise only slowly-accessible sorption sites.
2. Reaction kinetics inferred from concentration-distance profiles in soil columns with the soil solution stationary, as here, were more realistic.
3. The numerical model developed here, allowing for the effects of concentration, pH, CO_2 pressure and time on U adsorption and desorption, correctly predicted the measured U concentration-distance profiles.
4. Because all the model parameters were measured or otherwise estimated independently of the concentration-distance profiles, this indicated that the model correctly accounted for all the important processes.

5. A sensitivity analysis of the model indicated that the important effects to be allowed for in modelling U uptake by plant roots were the effects of pH, CO_2 pressure and organic and inorganic ligands on U speciation and sorption, and the effects of sorption kinetics.

Supporting information

A. Maximum U influx into roots because of mass flow.

Table S1 Maximum U influx into roots due to mass flow.

B. Uranium speciation in solution.

Figure S1. Uranium speciation in solution.

C. Further results

Figure S2. Measured and calculated concentration-distance profiles of Br.

Figure S3. Measured and calculated concentration-distance profiles of U at pH 6.0.

Figure S4. Measured and calculated concentration-distance profiles of U at pH 7.0.

Figure S5. Measured and calculated concentration-distance profiles of U at pH 7.6.

Copies of the experimental data and the program for the model are available from https://doi.org/10.17862/cranfield.rd.7093574/.

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444 **Table 1** Nomenclature.

Symbol	Meaning	Units
C	concentration of U or Br in the whole soil	mol dm^{-3} (soil)
C_L	concentration of all U species in the soil solution	mol dm^{-3} (solution)
C_{S1}	concentration of fast-reacting U in the soil solid	mol kg^{-1} (solid)
C_{S2}	concentration of slow-reacting U in the soil solid	mol kg^{-1} (solid)
D	diffusion coefficient in soil	dm^2 s^{-1}
D_L	diffusion coefficient in free solution	dm^2 s^{-1}
f	diffusion impedance factor	
$[ion]_L$	concentration of ion in the soil solution where ion = U species, Ca^{2+}, L^-, Cl^-	mol dm^{-3} (solution)
$K_{S,UO_2^{2+}}$	equilibrium constant for fast sorption of UO_2^{2+} (Equation 14)	mol dm^{-3} (solution)
$K_{S,CaUO_2(CO_3)_3^{2-}}$	equilibrium constant for fast sorption of $CaUO_2(CO_3)_3^{2-}$ (Equation 15)	mol dm^{-3} (solution)
k_1, k_2	forward, backward rate constants for slow U sorption	s^{-1}
P_{CO_2}	CO_2 pressure in soil air	kPa
S1	concentration of fast-reacting U sorption sites in the soil solid	mol kg^{-1} (solid)
t	time	s
x	distance	dm
θ	soil volumetric moisture content	
ρ	soil bulk density	kg dm^{-3} (soil)

445

446 **Table 2** Amounts of U transferred between half-cell couples calculated from the amounts
447 accumulated in the sink cells in Figure 5. Data are means ± standard errors (n = 3).

pH	U transferred (mol $\times 10^{-7}$)	
	P_{CO_2} = 1.3 kPa	P_{CO_2} = 6.5 kPa
6.0	0.75 ± 0.07	0.90 ± 0.07
7.0	3.84 ± 0.74	10.80 ± 1.87
7.6	15.10 ± 1.46	24.50 ± 8.29

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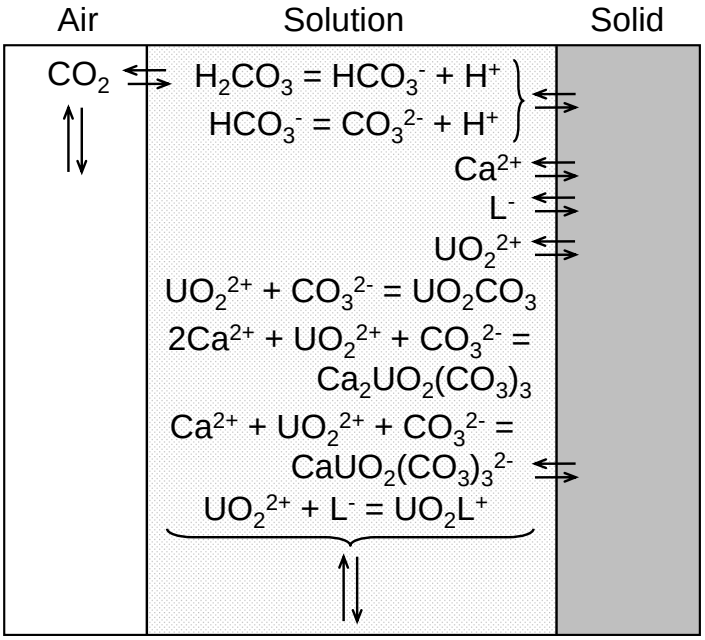


Figure 1 Speciation and sorption reactions controlling uranium diffusion in soil. Horizontal arrows indicate air–solution and solid–solution interchanges; vertical arrows indicate diffusion in the soil air and solution. Uranium species can diffuse in the soil solution but only very slowly in the soil solid.

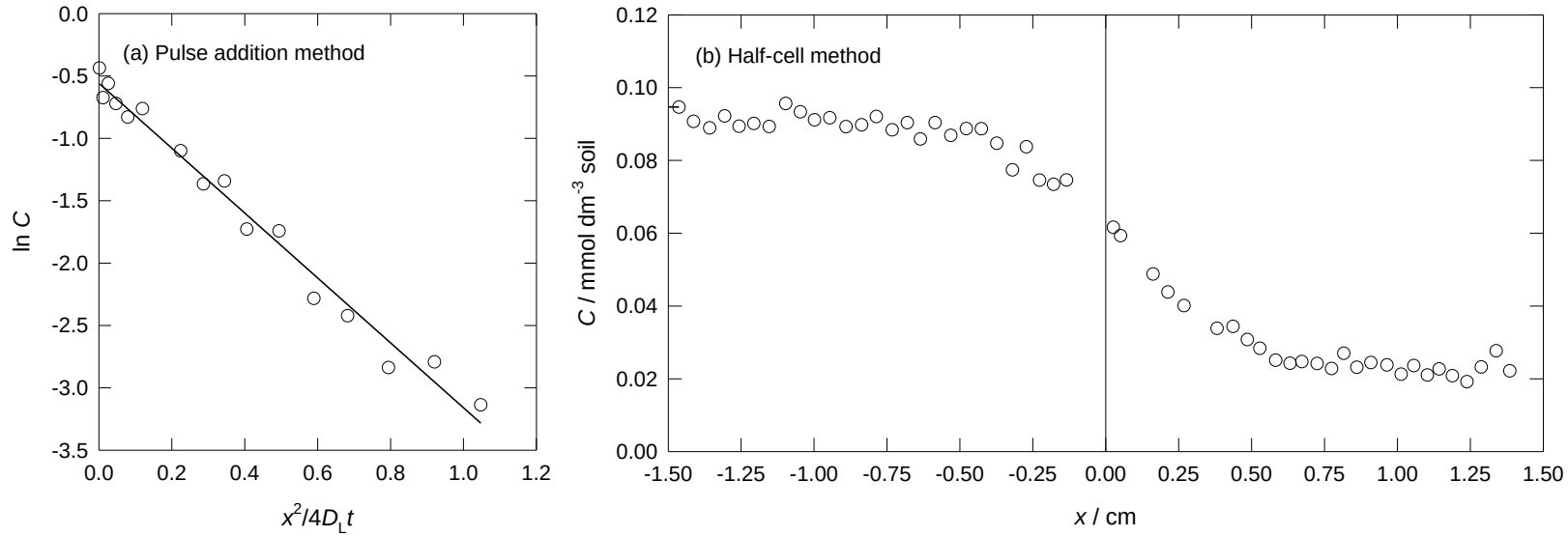
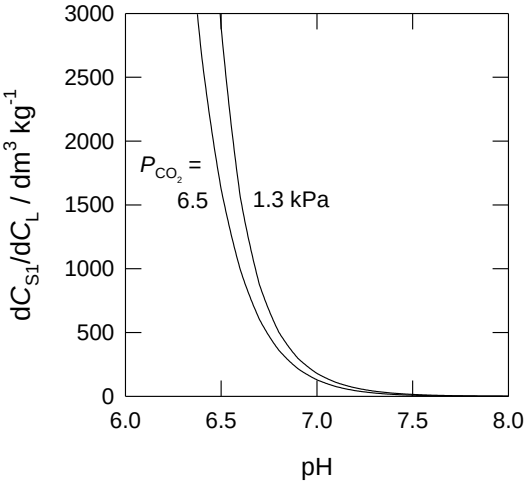


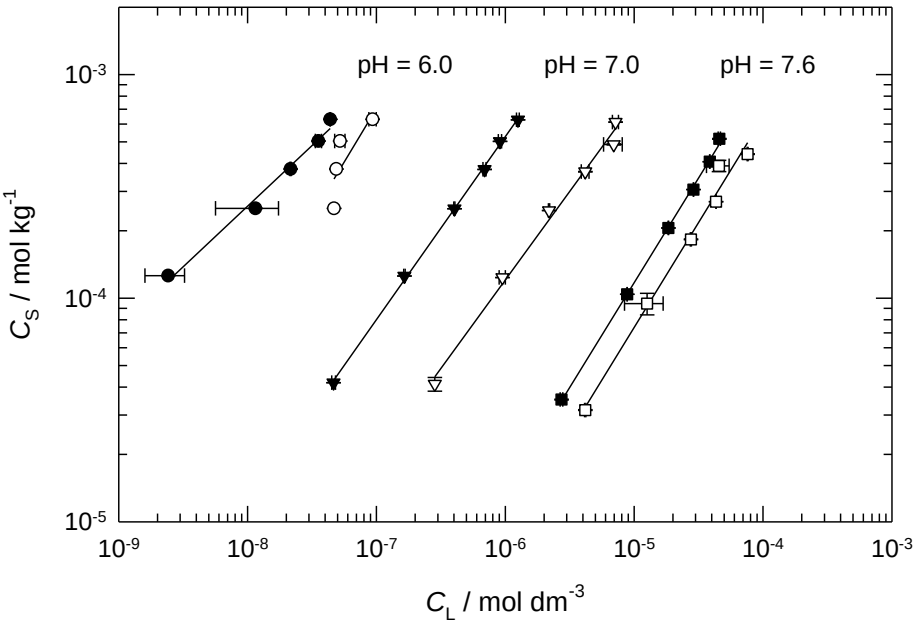
Figure 2 Concentration-distance profiles for Br^- diffusion in the experimental soil under the conditions of the main experiment. (a) For a pulse addition of Br^- at one end of a soil cell ($x = 0$); the points are measured data and the line is the fit to Equation (19) giving $f = 0.39$. (b) For two half-cells of soil containing different initial concentrations of Br; the line is the fit to Equation (17) using $f = 0.39$. Soil bulk density, $\rho = 1.42$ kg dm^{-3}; volumetric moisture content, $\theta = 0.36$; $D_L = 2.0 \times 10^{-7}$ dm^2 s^{-1}.



461

462 **Figure 3** Effect of pH and P_{CO_2} on the buffer power $b = dC_{S1}/dC_L$ for fast U sorption.

463



464

	Ambient air			5% CO_2 in air		
	pH = 6.0	pH = 7.0	pH = 7.6	pH = 6.0	pH = 7.0	pH = 7.6
m	3.86	43.74	5.60	149.2	5.47	3.27
n	0.523	0.818	0.936	0.764	0.775	0.928
R^2	0.92	1.00	1.00	0.60	0.98	0.97

465 **Figure 4** Uranium sorption measured in shaken soil suspensions. Closed symbols are at ambient
466 CO_2 pressure; open symbols at 5% CO_2 in air. Data are means ± SE; lines are fits of the data to C_S =
467 mC_L^n with the coefficients *m* and *n* as shown in the table.

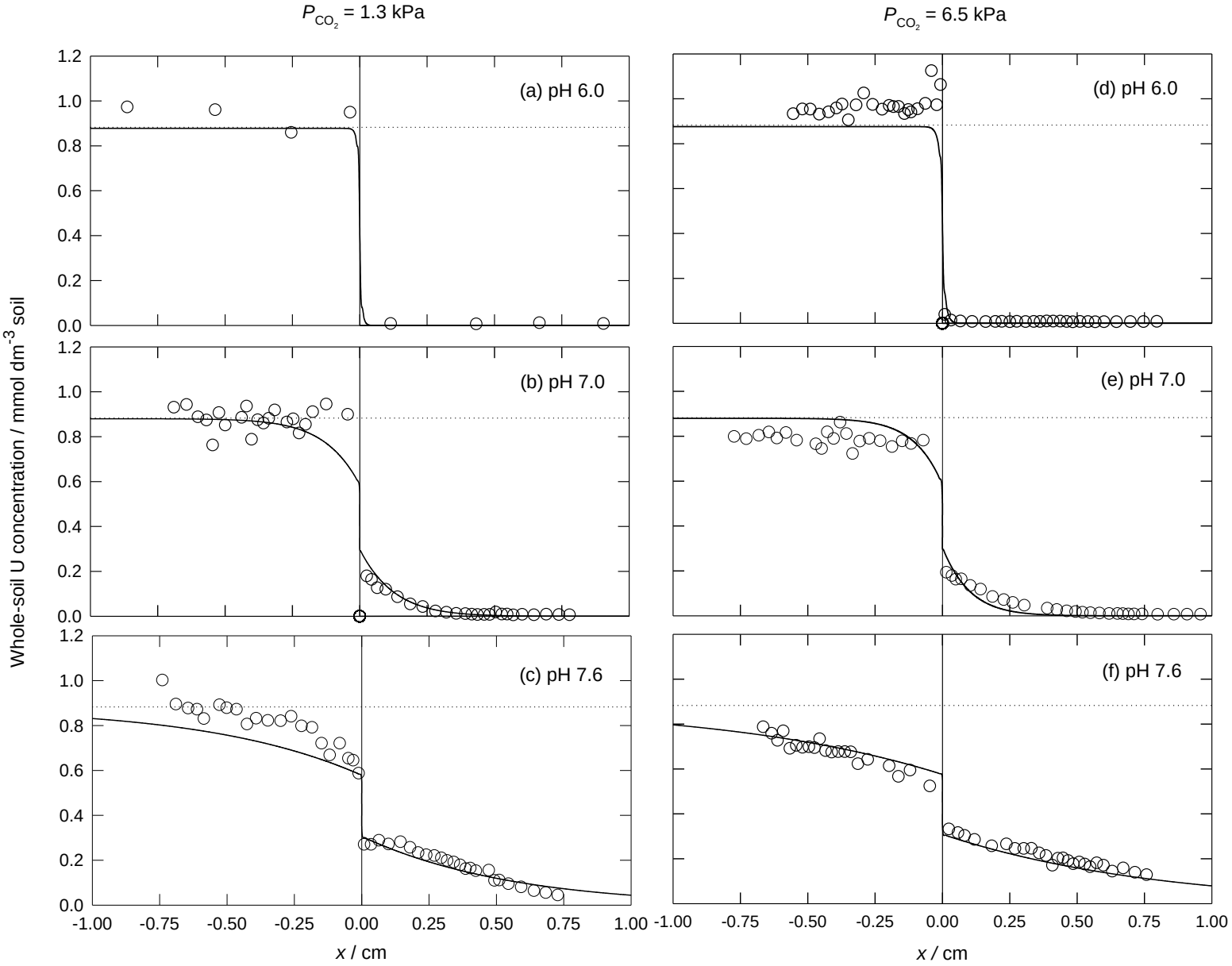
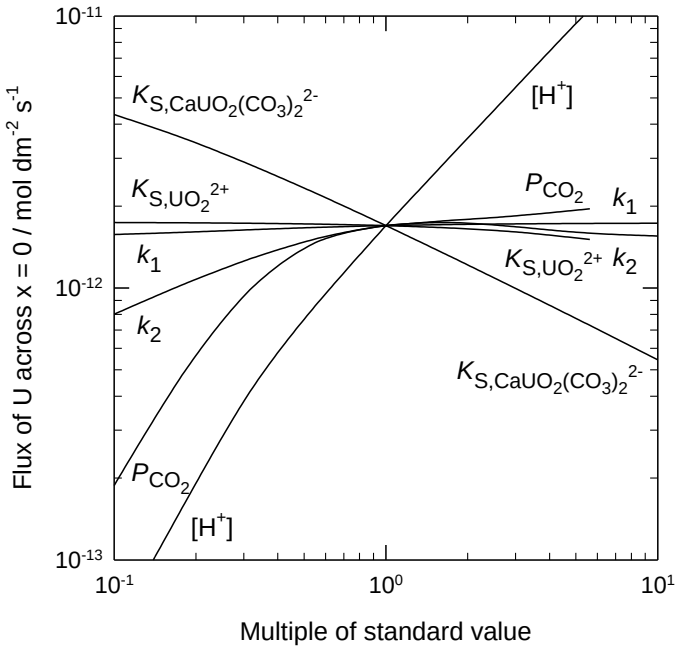


Figure 5 Concentration-distance profiles of U after diffusion between two half-cells of soil, one initially with and the other without added U. Points are observed data for a single replicate (Figures S3–S5, Supplementary Information, show all replicates); solid lines are calculated with the model; dashed lines are added U. (a)–(c) P_{CO_2} (CO_2 pressure) = 1.3 kPa and indicated pHs. (d)–(f) P_{CO_2} = 6.5 kPa and indicated pHs.



472

473 **Figure 6** Sensitivity of the model to its input parameters. Each of the indicated parameters was
474 varied in turn with the other parameters at their standard values. pH = 7.0; other standard parameter
475 values as for Figure 4. $K_{S,UO_2^{2+}}$, $K_{S,CaUO_2(CO_3)_3^{2-}}$ = equilibrium constants for sorption of UO_2^{2+},
476 $CaUO_2(CO_3)_3^{2-}$; k_1, k_2 = forward, backward rate constants for slow U sorption; P_{CO_2} = CO_2 pressure
477 in the soil air; $[H^+]$ = initial H^+ concentration in the soil solution.



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Uranium diffusion and time-dependent adsorption–desorption in soil: a model and experimental testing of the model

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