

CRANFIELD UNIVERSITY

JANA DARMOVZALOVÁ

TRANSPORT PROCESSES CONTROLLING URANIUM UPTAKE
BY PLANTS

SCHOOL OF WATER, ENERGY, ENVIRONMENT

PhD in Environment and Agrifood
Academic Year: 2015 - 2018

Supervisor: Prof. Guy J. D. Kirk
Associate Supervisor: Prof. Wilfred Otten
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ABSTRACT

The mechanisms of uranium (U) uptake by plants growing in contaminated soils are poorly understood, constraining the development of mitigation measures and models of U fate and behaviour. Uptake involves a complex interaction between diffusion and reaction processes in the rhizosphere, and root-induced changes in the soil affecting these processes. This thesis is concerned with developing better understanding of these processes, as represented in predictive mathematical models. Most past research on U transport and reaction in soils has been in shaken suspensions or flow-through systems, in which the rate-limiting processes are artificially altered. This thesis develops a novel experimental approach in which diffusion and reaction are measured simultaneously in soil with stationary pore water, better representing the rhizosphere. Concentration-distance profiles of U were measured between two half-cells of soil, one of which initially contained U and the other not, giving rates of desorption in the source and adsorption in the sink cell. The effects of typical root-induced changes in soil pH and CO₂ pressure were measured. Two models were compared: (a) an analytical solution of the appropriate diffusion equation with a constant diffusion coefficient, and (b) a numerical solution allowing for time- and concentration-dependent diffusion. The model parameters were measured or otherwise estimated independent of the concentration-distance profiles. The simple analytical solution correctly accounted for the effects of pH and CO₂ pressure on U diffusion, but under-predicted the diffusive flux. The numerical model correctly predicted the flux and concentration-distance profiles, including a discontinuity at the source-sink boundary due to differences in the kinetics of desorption and adsorption. The results show the importance of correctly allowing for the effects of pH, CO₂ pressure and sorption kinetics in modelling U uptake by plant roots. The model should be further corroborated in mesocosm, half-cell and field experiments, and by verifying U speciation.

Keywords: diffusion, uranium, soil modelling, radionuclide uptake, rhizosphere processes

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TABLE OF CONTENTS

ABSTRACT	i
ACKNOWLEDGEMENTS	iii
TABLE OF CONTENTS	v
LIST OF FIGURES	ix
LIST OF TABLES	xi
LIST OF EQUATIONS.....	xii
LIST OF SYMBOLS.....	xii
CHAPTER ONE.....	1
Review of U biogeochemistry in the rhizosphere: Experimental studies and modelling of U transport processes under the influence of plant root activity.....	1
1.1 Project background	1
1.2 Aims and objectives.....	2
1.3 Thesis structure.....	3
1.4 Review of U biogeochemistry in the rhizosphere: Experimental studies and modelling of U transport processes under the influence of plant root activity.....	6
1.4.1 Uranium in the environment.....	6
1.4.2 Elemental uranium.....	9
1.4.3 Uranium geochemistry	10
1.4.4 Biotic controls of U speciation and transport	17
1.4.5 Transport and reaction processes in soils	28
1.4.6 Measurement of uranium diffusion and reaction in soil.....	33
1.4.7 Modelling of uranium diffusion and reaction in rhizosphere	40
1.4.8 Chapter conclusions.....	44
CHAPTER TWO.....	47
Comparison of methods for measuring solute diffusion coefficients in soil	47
Summary.....	47
2.1 Introduction	48
2.2 Materials and methods.....	51
2.2.1 Preparation of diffusion cells.....	51
2.2.2 Pulse-addition method	52
2.2.3 Half-cell method	53

2.3 Results	54
2.3.1 Pulse-addition method	54
2.3.2 Half-cell method	57
2.4 Discussion.....	58
2.4.1 Methods comparison	58
2.4.2 Methodological considerations.....	60
2.5 Conclusions	61
CHAPTER THREE	62
Measurement of uranium sorption in shaken suspensions	62
Summary.....	62
3.1 Introduction	63
3.1.1 Background.....	63
3.2 Materials and methods.....	64
3.2.1 Speciation modelling.....	64
3.2.2 Shaken suspension experiments	65
3.2.3 Sorption kinetics.....	66
3.2.4 Data analysis.....	67
3.3 Results	68
3.3.1 Uranium speciation.....	68
3.3.2 Soil-solution partitioning of U.....	69
3.3.3 Sorption kinetics.....	72
3.3.4 Diffusion modelling.....	73
3.4 Discussion.....	75
3.4.1 Effect of pH and CO ₂ pressure	75
3.4.2 Effect of U concentration	76
3.4.3 Sorption kinetics.....	76
3.4.4 Diffusion modelling.....	77
3.5 Conclusions	78
CHAPTER FOUR	80
Uranium diffusion and time-dependent adsorption-desorption in soil: a model and experimental testing of the model	80
Foreword.....	80

Uranium diffusion and time-dependent adsorption-desorption in soil: a model and experimental testing of the model	81
Introduction	83
Materials and methods.....	89
Results and discussion	93
CHAPTER FIVE	108
General discussion and conclusions	108
5.1 Measurement of solute diffusion in soil	109
5.2 Measurements of U solid-solution partitioning.....	110
5.2.1 Effect of pH and CO ₂ pressure	110
5.2.2 Effect of U concentration	111
5.2.3 Sorption kinetics.....	111
5.3 Model of U diffusion and reaction	112
5.4 Further model development.....	113
5.5 Conclusions	114
5.5.1 Experimental methodology	114
5.5.2 Modelling	114
5.5.3 Future work.....	115
REFERENCES	118
APPENDICES	144
APPENDIX A.....	135
A-1 Test of homogeneous soil packing and volumetric moisture content throughout the soil column.....	144
A-2 Rejected replicates in pulse-addition method	145
B-1 Determination of U sorption equilibration time	147
B-2 Further results	148
B-3 Statistical analysis	150
B-3.1 One sample t-test for sorption kinetics experimental data	150
B-3.2 One way ANOVA for sorption kinetics experimental data.....	152
A. Supporting Information.....	155
B. Further methods.....	157

C. Further results	158
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LIST OF FIGURES

CHAPTER 1

Figure 1-1 Flow diagram of thesis organisation..	5
Figure 1-2 Topsoil uranium atlas of England and Wales.....	8
Figure 1-3 Decay series of ^{238}U	9
Figure 1-4 Biological and abiotic processes that affect the redox state of U.....	11
Figure 1-5 Uranium (VI) speciation diagram.....	16
Figure 1-6 Schematic representation of major processes in the rhizosphere.....	20
Figure 1-7 Approximate expression of the diffusion coefficient in soil Equation 1-5, and of the soil-solution concentration profile near the root.	31

CHAPTER 2

Figure 2-1. Concentration-distance profiles of Br^- (C) following a pulse addition of Br^- to one end of a moist soil column.	55
Figure 2-2. Concentration-distance profiles of Br^- from Figure 2-1 plotted according to Equation (2-4)..	55
Figure 2-3. Sensitivity of fitted f -values to the assessment of background concentration values and outliers for (a) Rep 1 and (b) Rep 2.	56
Figure 2-4. Concentration-distance profiles of Br^- through soil measured by the half-cell method..	57
Figure 2-5. The $f = 0.19$ from half-cell fitted to Equation (2-4)...	58

CHAPTER 3

Figure 3-1. Distribution diagram of U species.....	68
Figure 3-2. Uranium sorption measured in shaken soil suspensions.	69

Figure 3-3 Concentration-dependence of soil U buffer power for the studied U concentration range.	71
Figure 3-4 Sorption kinetics over 216 h equilibration measured in shaken suspensions.	72
Figure 3-5 Predicted concentration-distance profiles of U after diffusion between two half-cells of soil, one initially with and the other without added U as in Chapter 4.	74

CHAPTER 4

Figure 1 Speciation and sorption reactions controlling uranium diffusion in soil.	557
Figure 2 Concentration-distance profiles for Br ⁻ diffusion in the experimental soil under the conditions of the main experiment.	98
Figure 3 Effect of pH and P_{CO_2} on the buffer power $b = dC_{S1}/dC_L$ for fast U sorption.	99
Figure 4 Uranium sorption measured in shaken soil suspensions.	100
Figure 5 Concentration-distance profiles of U after diffusion between two half-cells of soil, one initially with and the other without added U.	101
Figure 6 Sensitivity of the model to its input parameters.	102

LIST OF TABLES

CHAPTER 1

Table 1-1 Economically important uranium minerals..... 6

Table 1-2 Formation constants for some of the U(VI) species in solution. 12

CHAPTER 3

Table 3-1 Comparison of soil U buffer powers calculated from the shaken suspension data and Equation 3-6 with those derived from the diffusion and reaction model in Chapter 4.....73

CHAPTER 4

Table 1 Nomenclature.97

Table 2 Amounts of U transferred between half-cell couples calculated from the amounts accumulated in the sink cells in Figure 5.....98

LIST OF EQUATIONS

CHAPTER 1

(1-1)	11
(1-2)	21
(1-3)	29
(1-4)	29
(1-5)	29
(1-6)	30
(1-7)	30
(1-8)	30
(1-9)	31
(1-10)	31
(1-11)	32
(1-12)	32
(1-13)	33
(1-14)	33
(1-15)	41

CHAPTER 2

(2-1)	49
(2-2)	49
(2-3)	50
(2-4)	50
(2-5)	50
(2-6)	51

CHAPTER 3

(3-1)	63
(3-2)	66
(3-3)	67

(3-4)	67
(3-5).....	70
(3-6).....	70

CHAPTER 4

(1).....	82
(2).....	82
(3).....	82
(4).....	82
(5).....	82
(6).....	83
(7).....	83
(8).....	83
(9).....	83
(10).....	83
(11).....	84
(12).....	84
(13).....	84
(14).....	84
(15).....	84
(16).....	84
(17).....	85
(18).....	86
(19).....	86

LIST OF ABBREVIATIONS

Al ³⁺	Aluminium ion
AM fungi	Arbuscular mycorrhizal fungi
ANOVA	Analysis of variance
AQDS	9, 10-anthraquinone-2, 6-disulfonic acid
AQDS	Reduced form of AQDS
Ar	Argon
ATSDR	Agency for Toxic Substances and Disease Registry
BCR	Community Bureau of Reference
Br ⁻	Bromide ion
Ca(OH) ₂	Calcium hydroxide
Ca ²⁺	Calcium ion
CaBr ₂	Calcium bromide
CaCl ₂	Calcium chloride
CEC	Cation exchange capacity
Cl	Chlorine
Cl ⁻	Chloride ion
CO ₂	Carbon dioxide
CO ₃ ²⁻	Carbonate ion
Defra	Department for Environment, Food & Rural Affairs (GOV. UK)
DGT	Diffusive gradient in thin films
DU	Depleted uranium

EA	Environment Agency
EJSS	European Journal of Soil Science
EPA	United States Environmental Protection Agency
FA	Fulvic acid
GC	Gas chromatography
GRG	Generalized Reduced Gradient (MS Excel Solver algorithm)
H ⁺	Hydrogen ion
H ₂ CO ₃ ⁻	Carbonic acid
H ₂ O	Dihydrogen oxide (water)
H ₂ PO ₄ ⁻	Dihydrogenphosphate
HCO ₃ ⁻	Bicarbonate ion
ICP-MS	Inductively coupled plasma mass spectrometry
IL, USA	Illinois, USA
Lo-Rise	Long-lived radionuclides in the surface environment
M ⁺	Metal cation
MA, USA	Massachusetts, USA
Mg ²⁺	Magnesium ion
Na	Sodium
Na ⁺	Sodium ion
NaHCO ₃	Sodium bicarbonate
NaNO ₃	Sodium nitrate
NDA-	Nuclear Decommissioning Authority's Radioactive Waste Management

RWMD	Directorate
NERC	Natural Environment Research Council
NH_4^+	Ammonium chloride
NH_4Cl	Ammonium chloride
$\text{NH}_4\text{-N}$	Nitrogen content of the ammonia
NH_4NO_3	Ammonium nitrate
NO_3^-	Nitrate ion
$\text{NO}_3\text{-N}$	Nitrogen content of nitrate
NOM	Natural organic ligands
NY	New York
OC	Organic matter content
$\text{OC}_{\text{oxidised}}$	Oxidised organic carbon
$\text{OC}_{\text{reduced}}$	Reduced organic carbon
OH^-	Hydroxide ion
Ra	Radon
RATE	Radioactivity and the Environment
RSD	Relative standard error
SCM	Surface complexation model
Sd	standard deviation
SE	Standard error
SEM	Scanning electron microscopy
SiCSA	Single-cell sampling-and-analysis

SO_4^{-2}	Sulphate
Sr	Strontium
SRB	Sulphate-reducing bacteria
SSA	Specific surface area
SSD	Sum of squared deviations
STD	Standard mode (ICP-MS)
TF	Transfer factors
U	Uranium
U(IV)	Tetravalent uranium
U(VI)	Hexavalent uranium
U.S.	United States of America
U_3O_8	Triuranium octoxide
UK	United Kingdom
UO_2^{2+}	Uranyl ion
UO_2CO_3	Uranyl carbonate
UO_3	Uranium (tri)oxide
USA	United States of America
WA, USA	Washington, USA
WHO	World Health Organization
Zn	Zinc

LIST OF SYMBOLS

Symbol	Definition	Units
$\equiv\text{Fe}$	Surface-bound iron	
B	Solute buffer power, dC/dC_L	
C	Concentration of diffusible solute in the whole soil	mol dm^{-3} (soil)
C_0	Initial sink concentration	mol dm^{-3} (soil)
C_1	Initial source concentration	mol dm^{-3} (soil)
C_{DGT}	DGT measured concentration	
C_L	Concentration of solute in the soil solution	mol dm^{-3} (solution)
C_s	Concentration of solute in the soil solid	mol kg^{-1} (solid)
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	$\text{dm}^2 \text{s}^{-1}$
D_L	Diffusion coefficient in free solution	$\text{dm}^2 \text{s}^{-1}$
D_s	Surface diffusion coefficient	$\text{dm}^2 \text{s}^{-1}$
E	Activation energy	$\text{kJ mol}^{-1} \text{K}^{-1}$
F	Flux	$\text{mol m}^{-2} \text{s}^{-1}$
F	Diffusion impedance factor	
F'	Faraday constant	$\text{J mol}^{-1} \text{V}^{-1}$
$[\text{ion}]_L$	Concentration of ion in the soil solution where ion = U species, Ca^{2+} , L^- , Cl^-	mol dm^{-3} (solution)

K_a	Surface area normalised K_D	
K_D	Distribution coefficient	$\text{dm}^3 \text{kg}^{-1}$
$K_{\text{S1CaUO}_2^{2+}(\text{CO}_3)_3^{2-}}$	Equilibrium constant for fast sorption of UO_2^{2+} (Equation 14)	mol dm^{-3} (solution)
$K_{\text{S1CaUO}_2^{2+}}$	Equilibrium constant for fast sorption of $\text{CaUO}_2(\text{CO}_3)_3^{2-}$ (Equation 15)	mol dm^{-3} (solution)
k_1, k_2	Forward, backward rate constants for slow U sorption	s^{-1}
L^-	Organic ligands	
M	Freundlich isotherm parameter	
M^+	Metal cation	
n	Freundlich isotherm parameter	
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)
R	Reaction rate	
R	Universal gas constant	J mol^{-1}
T	Time	s
T	Absolute temperature	$^{\circ}\text{K}$
X	Distance	dm
Z_A	Charge of the ion A	
θ	Soil volumetric moisture content	
ψ	Potential	
ρ	Bulk density	kg dm^{-3} (soil)

CHAPTER ONE

Review of U biogeochemistry in the rhizosphere: Experimental studies and modelling of U transport processes under the influence of plant root activity

1.1 Project background

Radionuclides exist in the environment as part of natural composition of the geosphere. However, their concentrations can be significantly enhanced due to human activity such as mining or nuclear waste disposal. The movement of these potentially dangerous chemicals through the soil into hydrological and biological systems can lead to exposure to local populations, both human and other species. This is of special interest with respect to uranium, U, because of its radioactivity and chemical toxicity.

Transport of radionuclides, including U, through the soil involves a combination of convection and diffusion. In most situations, diffusion plays the major role and is relevant to the transfer of radionuclides into plants (Marschner, 2012). Uranium transport through soil is accompanied by simultaneous reactions with soil solid surfaces. These reactions are complicated because U exists in the soil solution as a large number of different species, and the relative concentrations of the species vary with the concentrations of other reactants and, particularly, the soil pH and CO₂ pressure (Cumberland *et al.*, 2016; Tinnacher *et.al.*, 2013; Liu *et al.*, 2011; Liu *et al.*, 2013).

The sorption reaction rates may also be slower or faster compared to rates of diffusion through the soil. Commonly, reaction rates and equilibria are studied in suspensions of soil with solutions that are shaken to remove transport limitations. Further, this is often done with pure soil components, as opposed to true soils. The application of results so obtained to real soil systems is highly uncertain. A central idea in this thesis is to study U transport and reaction simultaneously, and to use the well-developed theory of transport processes in soils to separate transport from reaction and thereby to obtain true reaction rates and equilibria for understanding real soil systems.

This PhD project aimed to investigate U transport and reactions in soils as they affect uptake by roots. The approach was to design experiments based on diffusive

transport through soils in the absence of plant roots, but with the effects of root-induced changes in the soil (changes in pH and CO₂ pressure) artificially introduced. Understanding these transport and reaction processes limits the development of realistic models of U uptake by plants, with which to investigate risks of soil U contamination. The experimental findings provide the basis for formal testing of a mechanistic model of U transport and uptake by plants developed in parallel by Boghi *et al.* (2018).

This PhD project and model development was part of a larger consortium project led by the University of Manchester called Lo-Rise – ‘Long-lived radionuclides in the surface environment - mechanistic studies of speciation, environmental transport and transfer’, which was part of the ‘Radioactivity and the Environment’ (RATE) programme sponsored by the Natural Environment Research Council (NERC), the Environment Agency (EA) and the Nuclear Decommissioning Authority’s Radioactive Waste Management Directorate (NDA-RWMD).

The Lo-Rise project involved a range of field, laboratory and modelling research on the physical, chemical and biological processes that govern radionuclide transport through soils and sediments and into biota.

1.2 Aims and objectives

The overall aims were

- to understand the processes controlling transport of U through soil and its simultaneous solid-solution interchange, especially as influenced by plant-induced changes in soil chemistry, and
- to use this understanding to improve and test a mechanistic model of U transport and uptake by plants developed by Boghi *et al.* (2018).

The specific objectives towards these aims were

- to develop methods for measuring solute diffusion in soils,
- to measure and characterise the effects of pH and CO₂ pressure and time on U reactions in soil,

- to measure U diffusion and reactions in soil as influenced by pH and CO₂ pressure and time,
- To test the mechanistic model of U transport and uptake by plants against experimental measurements.

1.3 Thesis structure

This thesis is organised in five chapters. Chapter 1 gives a general introduction and literature review to justify the basis and purpose of this study. The literature review is part of the justification. Chapter 2 presents method development for measurement of solute simultaneous diffusion and reaction (applied in Chapter 4). The method development was done by comparison of two methods where non-reactive solute diffuses through soil blocks. At the same time, the diffusion parameter and soil impedance factor were determined. Chapter 3 considers U sorption processes in soil as affected by root-induced changes in pH and CO₂ pressure. This is achieved by measurement of U solid-solution partitioning in shaken suspensions. Chapter 4 describes a mechanistic model of U transport and reaction in the rhizosphere (developed elsewhere in the Lo-Rise project, as previously discussed) and experimental testing of the model through (a) experimental U concentration-distance profiles as measured using methods developed in Chapter 2, and (b) independently measured or estimated model input parameters. This chapter has been submitted for publication in *European Journal of Soil Science* (EJSS). The submitted manuscript is presented unchanged. Finally, general discussion of all the findings from previous chapters and conclusions drawn are given in Chapter 5.

The Appendix contains supporting information for findings from all chapters. Appendix A gives further details of methods development corresponding to Chapter 2. This includes soil packing method development and rejected replicates of impedance factor measurement. In appendix B, further sorption experimental data are provided, including statistical analysis of the results. Appendix C corresponds to Chapter 4 and includes resulting concentration-distance profiles of all replicate runs from U diffusion measurement and fits from the mechanistic model of Boghi *et al.* (2018). In addition,

Appendix C includes Supporting information, as submitted for publication in the EJSS. Figure 1-1 shows the flow diagram of the thesis organisation.

The research was presented orally at 3rd European Radiological Protection Research Week in Rovinj, Croatia (October 2018).

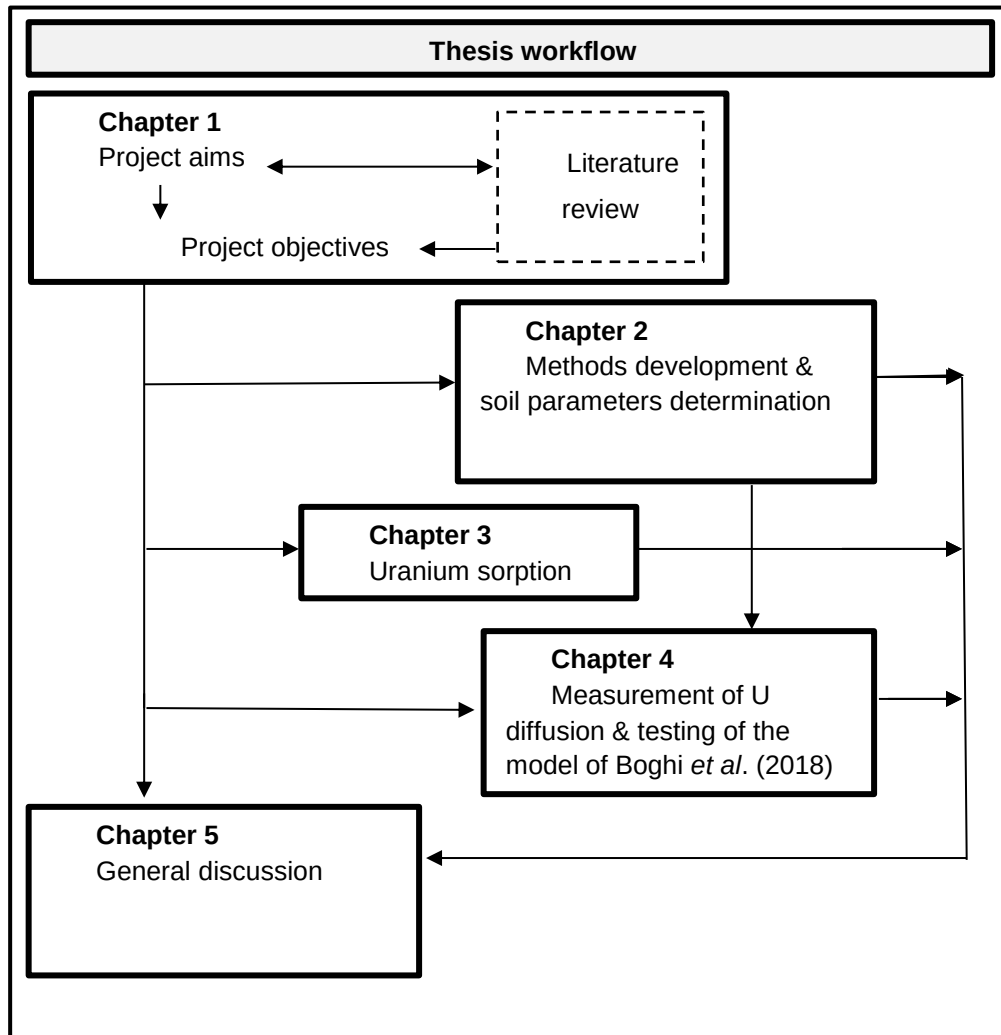


Figure 1-1. Flow diagram showing the thesis structure. The arrows indicate the flow of ideas and links between the chapters.

1.4 Review of U biogeochemistry in the rhizosphere: Experimental studies and modelling of U transport processes under the influence of plant root activity

Introduction

1.4.1 Uranium in the environment

Radionuclides exist in the subsurface environment as part of natural composition of the geosphere. However, their concentrations can be significantly enhanced by human activity. The movement of these potentially dangerous elements through the soil into the hydrological and biological systems can lead to exposure to local populations, both human and other species. Abundant use of U and its presence in the environment (Moore & Shackelford, 2011), long-life and potential damage to human health give this radionuclide (regardless its form, natural or depleted) special importance among other radionuclides, whether naturally occurring or man-made.

Table 1-1 Economically important uranium minerals (Bhargava *et al.*, 2015).

Mineral type	Mineral name	Formula	Typical %U
<i>Tetravalent uranium minerals (U^{4+})</i>			
Oxides	Uraninite	$(U_{1-x}^{4+}, U_x^{6+})O_2 + x$ [ideally UO_2]	46–88
	Pitchblende	UO_2 amorphous	86–88
REE $\pm$ Ti $\pm$ Fe-oxides	Brannerite	$(U,Ca,Y,Ce,La)(Ti,Fe)_2O_6$	26–44
	Betafite	$(Ca,U)_2(Ti,Nb,Ta)_2O_6(OH)$	15–24
	Davidite	$(La,Ce)(Y,U,Fe)(Ti,Fe)_{20}(O,OH)_{38}$	1–6
	Orthobrannerite	$U_2Ti_4O_{12}(OH)_2$	~53
Silicates	Coffinite	$U(SiO_4)_{1-x}(OH)_{4x}$	40–60
	Uranothorite	$(U,Th)SiO_4$	<10
<i>Hexavalent uranium minerals (U^{6+})</i>			
Phosphates	Autunite	$Ca(UO_2)_2(PO_4)_2 \cdot 10-12H_2O$	48–50
	Meta-autunite	$KCa(H_3O)_3(UO_2)_7(PO_4)_4O_4 \cdot 6-8H_2O$	~57
	Torbernite	$Cu(UO_2)_2(PO_4)_2 \cdot 8-12H_2O$	47
Vanadates	Carnotite	$K_2(UO_2)_2(VO_4)_2 \cdot 1-3H_2O$	53–55
	Tyuyamunite	$Ca(UO_2)_2(VO_4)_2 \cdot 5-8H_2O$	~52
Silicates	Boltwoodite	$HK(UO_2)SiO_4 \cdot 1.5H_2O$	~55
	Sklodowskite	$(H_3O)_2 Mg(UO_2)_2(SiO_4)_2 \cdot 4(H_2O)$	49–54
	Uranophane	$Ca(UO_2)_2(SiO_3)(OH)_2 \cdot 5H_2O$	~41

Uranium is a trace element found in soils at the average concentration of 2.6 mg kg^{-1} in the earth's crust (Plant *et al.*, 1999). There are over 100 different types of uranium ore (ATSDR, 1999). Uranium is most commonly found in its mixed oxide form U_3O_8 , as amorphous pitchblende or as a crystalline form uraninite (Craft *et al.*, 2004). The most economically important uranium-bearing minerals are listed in Table 1-1.

Uranium mining for industrial and military purposes, phosphorus fertiliser production and application, and nuclear waste disposal are typical pathways of U introduction into the environment. Uranium can be found in soils and dust, oceans and fresh water bodies, food and even drinking water. The 2006 Defra report on groundwater U presence states that out of 1556 analysed groundwater samples in Great Britain, only 0.71 % exceeded the WHO (2004) recommended maximum concentration of $15 \text{ } \mu\text{g L}^{-1}$. However, there are locations where up to $8000 \text{ } \mu\text{g L}^{-1}$ were measured, especially in Scandinavia and the United States of America (Smedley *et al.*, 2006).

In English and Welsh soils, elevated concentrations were found in various areas as shown in Figure 1-2 (Rawlins *et al.*, 2012). The reported values did not exceed 88 mg kg^{-1} but localised contamination may far exceed this value. For example, in South Terras, the closed uranium/radium mine in Cornwall, U activities in plants and sediments exceeded 80-160 times those as compared to background concentrations (Dean, 1966).

Canadian Soil Quality Guidelines for Uranium (2007) reports the average soil U concentrations at U deposits between $1 \text{ and } 500 \text{ mg kg}^{-1}$. This is in agreement with findings of Lloyd *et al.* (2009), who investigated a depleted uranium, DU, contaminated site at the DU factory in Colonie (NY, USA). The DU concentrations in the soil reached $\sim 500 \text{ mg kg}^{-1}$ as compared to a 1 mg kg^{-1} background concentration. In Kosovo, hot spot contamination was reported levels up to $\approx 18\,000 \text{ mg kg}^{-1}$ in areas of penetration with DU ammunition (Sansone *et al.*, 2001). In southern Iraq, the 2003 conflict left behind soil contamination from ammunition with DU concentrations reported as high as 3250 mg kg^{-1} (IAEA, 2010).

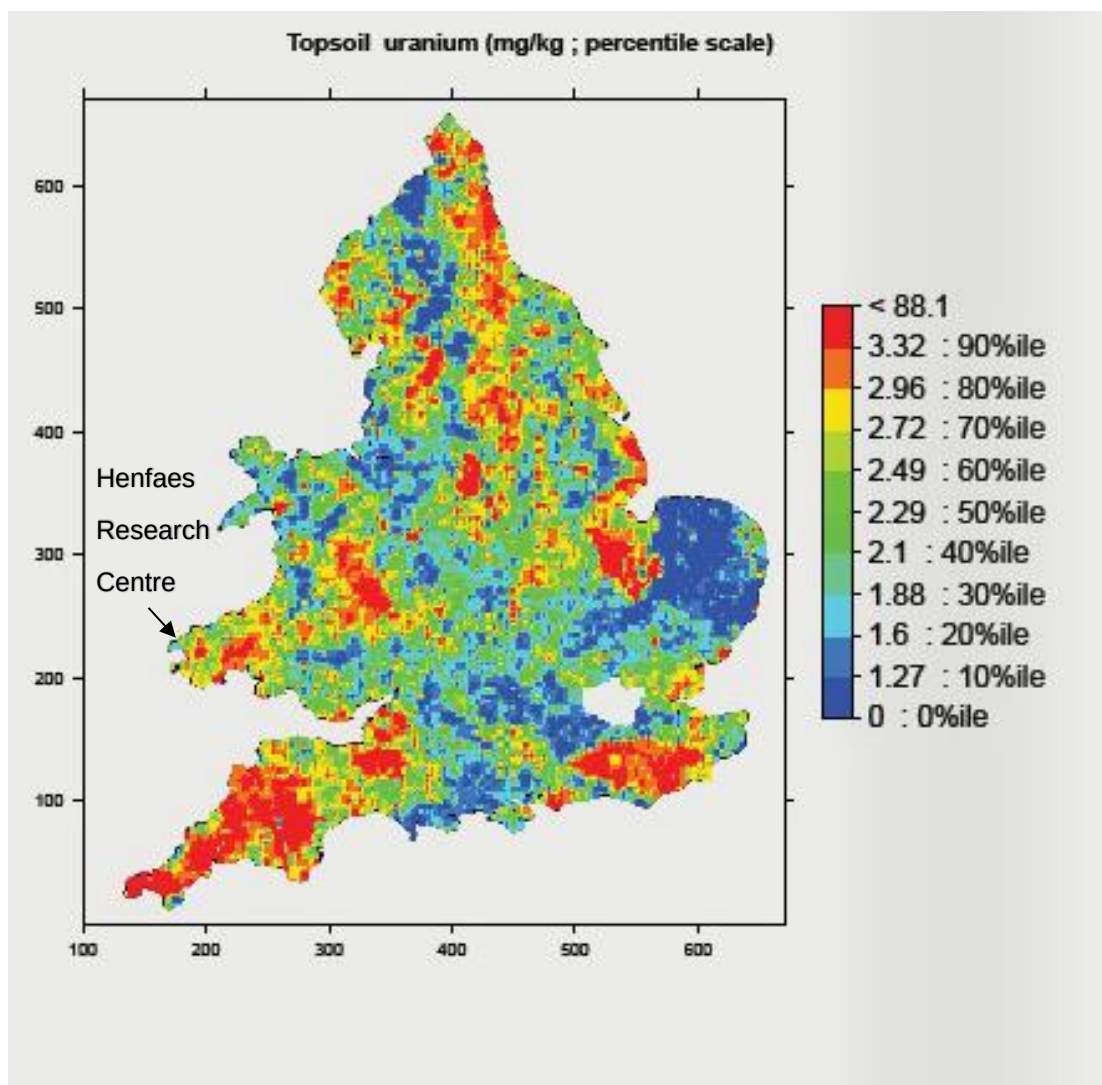


Figure 1-2 Topsoil uranium atlas of England and Wales (Rawlins *et al.*, 2012). The percentile scale intervals represent cumulative frequency distribution. Over 90% of the data are below 3.3 mg kg⁻¹ and only four samples were above 20 mg kg⁻¹. Maximum reported values were 88 mg kg⁻¹. Predictions are based on a 2.5 km by 2.5 km grid (therefore hotspots are neglected). Contains British Geological Survey materials © NERC (2015). The arrow indicates the experimental soil sampling location (Henfaes Research Centre, Bangor, Wales).

Food contamination originates from transfer of U from water and soil. It has been found in both crops (Amaral *et al.*, 2005; Chen *et al.*, 2005; Senila *et al.*, 2012) and wild plants (Thiry *et al.*, 2005) and also in livestock and other foodstuff (Anke *et al.*, 2009). The U radioactivity and chemical toxicity calls for a deeper understanding and evaluation of U mobility in the environment, especially in soils from where it can transfer into other spheres.

Although convection plays an important role in U long distance transport, diffusion is the governing process on the scale relevant to transfer of the radionuclides into plants (i.e., the entry gate into the food chain) (Tinker & Nye, 2000). Diffusion may be strongly affected by sorption and desorption processes resulting in either U immobilization in soil solid or easy transport in soil solution towards a plant root. Although U transport models exist (Tokunaga *et al.*, 2004a; Tokunaga *et al.*, 2004b; Kumar *et al.*, 2015; Curtis *et al.*, 2009; Pérez-Sánchez & Thorne, 2014a), they are often limited to empirical observations and are applicable only to the system studied. Therefore, there is a need to improve our understanding and modelling concepts of the transport of U through soils, as well as the mechanisms involved in its uptake by plants.

1.4.2 Elemental uranium

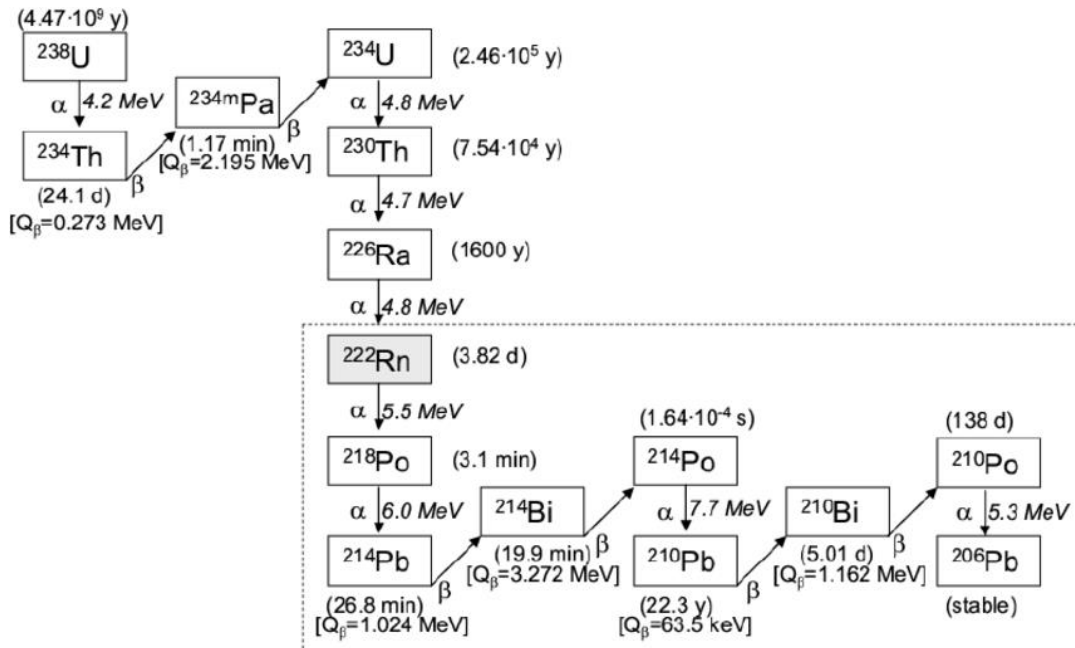


Figure 1-3 Decay series of ^{238}U (Argyriades *et al.*, 2009).

Uranium is a heavy metal from the actinide group. It has 16 known isotopes, of which all are radioactive (Markich, 2002). In natural environments, uranium exists only as three isotopes: ^{238}U (99.275%), ^{235}U (0.72%), and ^{234}U (0.005%), all are radioactive and alpha-emitters. The ^{238}U isotope has a half-life of 4.46 billion years (Rawlins *et al.*, 2012). The ^{238}U decay series is complex and production of alpha, beta and gamma radiation is involved (Figure 1-3) (Argyriades *et al.*, 2009).

The ^{235}U isotope has the highest radioactivity (seven-times more than ^{238}U) and therefore U enrichment is applied in fuel production for nuclear power plants (Chen & Yiaccoumi, 2002; Craft *et al.*, 2004). After the fuel is spent, depleted uranium remains. It has low radioactivity but its heavy metal toxicity is hazardous to the environment and human health. Natural and depleted U are known to result mainly in renal diseases but insoluble U compounds are also carcinogenic (Duquène *et al.*, 2006). For example, a number of studies showed that human lung cells can be a subject to malignant transformations after DU exposure, which can lead to development of lung cancer (Xie *et al.*, 2009; Wise *et al.*, 2007, Yang *et al.*, 2002).

1.4.3 Uranium geochemistry

1.4.3.1 Uranium chemistry in soils

Uranium speciation in soil solids and solution is complex. The dynamic nature of U speciation is governed by solid-solution system composition and environmental conditions, especially pH. Chemical behaviour of U is further dependent on processes such as sorption, colloid formation, precipitation and interaction with inorganic and organic ligands.

Uranium forms large ions of high charge which do not easily fit into crystal structure of common silicate minerals (e.g., feldspar, mica). Uranium has five oxidation states: +2, +3, +4, +5, and +6. However, only U(IV) and U(VI) are significant in the natural environment as all the other oxidation states are instable (Craft *et al.*, 2004).

The hexavalent form of uranium, U(VI), is the most common in oxic environments. The U(VI) is found principally as the linear uranyl moiety ($\text{O}=\text{U}=\text{O}$, or UO_2^{2+}), a soluble and mobile species in typical conditions of surface environments. In contrast, U(IV) has very low solubility and therefore reduced mobility (Reeder *et al.*, 2001).

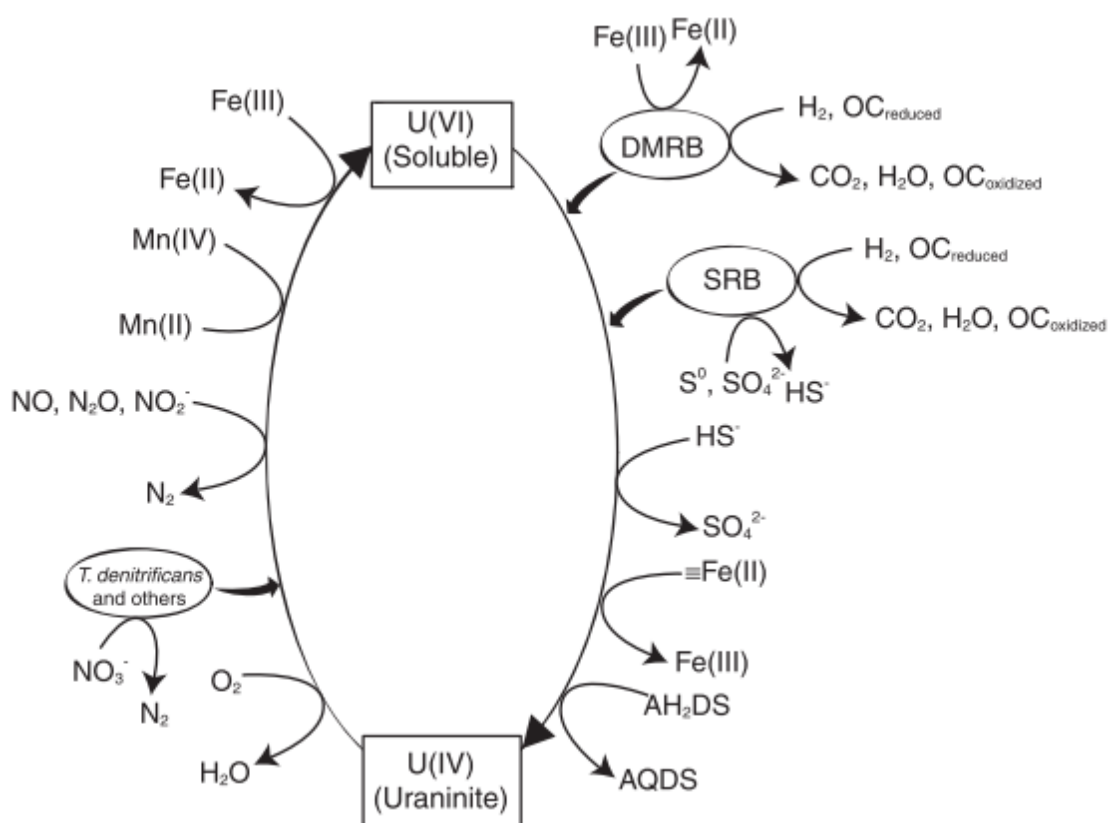


Figure 1-4 Biological (ovals) and abiotic processes that affect the redox state of U. DMRB = reduction by dissimilatory metal-reducing bacteria; SRB = sulfate-reducing bacteria; $\equiv\text{Fe}$ = surface-bound iron; $\text{OC}_{\text{reduced}}$ = reduced organic carbon; $\text{OC}_{\text{oxidised}}$ = oxidised organic carbon; AQDS = 9, 10-anthraquinone-2, 6-disulfonic acid; and AH_2DS is the reduced form of AQDS (Ginder-Vogel & Fendorf, 2007).

The soluble U species may be stabilised in soils by reduction of U(VI) to sparingly soluble U(IV). The reduction can be mediated by both abiotic and biotic processes. The U(IV) solubility is limited even in the presence of dissolved ligands which otherwise form relatively mobile species with U(VI). Figure 1-4 shows biogeochemical U redox transformations from its soluble U(VI) to its rather immobile U(IV) form (and vice versa). In general, electron donor compounds must be present to achieve U reduction according to the reaction:



Within the environment, uranium reduction may be reversed if stable redox conditions are disturbed. This may happen during extreme climate events (e.g. heavy

rains followed by soil erosion as a result of oxidation of previously anoxic soil) even where U is tightly bound to natural organic matter (NOM) or other strong sorbents. Reoxidation of U(IV) to U(VI) can therefore cause U remobilisation (Dong *et al.*, 2006).

Table 1-2 Formation constants ($\log \beta^*$) for some of the U(VI) species in solution (Davis *et al.*, 2004). The superscript ^a indicates values from Grenthe *et al.* (1992), unless otherwise indicated (Davis *et al.*, 2004).

Reaction	$\log \beta^*$ (I = 0) ^a
$\text{UO}_2^{2+} + \text{H}_2\text{O} \rightleftharpoons \text{UO}_2\text{OH}^+ + \text{H}^+$	-5.20
$\text{UO}_2^{2+} + 2\text{H}_2\text{O} \rightleftharpoons \text{UO}_2(\text{OH})_2(\text{aq}) + 2\text{H}^+$	-11.50 ^b
$\text{UO}_2^{2+} + 3\text{H}_2\text{O} \rightleftharpoons \text{UO}_2(\text{OH})_3^- + 3\text{H}^+$	-20.00 ^c
$\text{UO}_2^{2+} + 4\text{H}_2\text{O} \rightleftharpoons \text{UO}_2(\text{OH})_4^{2-} + 4\text{H}^+$	-33.0
$2\text{UO}_2^{2+} + \text{H}_2\text{O} \rightleftharpoons (\text{UO}_2)_2\text{OH}^{3+} + \text{H}^+$	-2.70
$2\text{UO}_2^{2+} + 2\text{H}_2\text{O} \rightleftharpoons (\text{UO}_2)_2(\text{OH})_2^{2+} + 2\text{H}^+$	-5.62
$3\text{UO}_2^{2+} + 4\text{H}_2\text{O} \rightleftharpoons (\text{UO}_2)_3(\text{OH})_4^{2+} + 4\text{H}^+$	-11.90
$3\text{UO}_2^{2+} + 5\text{H}_2\text{O} \rightleftharpoons (\text{UO}_2)_3(\text{OH})_5^+ + 5\text{H}^+$	-15.55
$3\text{UO}_2^{2+} + 7\text{H}_2\text{O} \rightleftharpoons (\text{UO}_2)_3(\text{OH})_7^- + 7\text{H}^+$	-31.00
$4\text{UO}_2^{2+} + 7\text{H}_2\text{O} \rightleftharpoons (\text{UO}_2)_4(\text{OH})_7^+ + 7\text{H}^+$	-21.9
$\text{UO}_2^{2+} + \text{CO}_3^{2-} \rightleftharpoons \text{UO}_2\text{CO}_3(\text{aq})$	9.67 ^d
$\text{UO}_2^{2+} + 2\text{CO}_3^{2-} \rightleftharpoons \text{UO}_2(\text{CO}_3)_2^{2-}$	16.94
$\text{UO}_2^{2+} + 3\text{CO}_3^{2-} \rightleftharpoons \text{UO}_2(\text{CO}_3)_3^{4-}$	21.60
$3\text{UO}_2^{2+} + 6\text{CO}_3^{2-} \rightleftharpoons (\text{UO}_2)_3(\text{CO}_3)_6^{6-}$	54.0
$2\text{UO}_2^{2+} + \text{CO}_3^{2-} + 3\text{H}_2\text{O} \rightleftharpoons (\text{UO}_2)_2\text{CO}_3(\text{OH})_3^- + 3\text{H}^+$	-0.86
$3\text{UO}_2^{2+} + \text{CO}_3^{2-} + 3\text{H}_2\text{O} \rightleftharpoons (\text{UO}_2)_3\text{CO}_3(\text{OH})_3^+ + 3\text{H}^+$	0.66
$\text{UO}_2^{2+} + \text{Cl}^- \rightleftharpoons \text{UO}_2\text{Cl}^+$	0.17
$\text{Ca}^{2+} + \text{UO}_2^{2+} + 3\text{CO}_3^{2-} \rightleftharpoons \text{CaUO}_2(\text{CO}_3)_3^{2-}$	25.4 ^e
$2\text{Ca}^{2+} + \text{UO}_2^{2+} + 3\text{CO}_3^{2-} \rightleftharpoons \text{Ca}_2\text{UO}_2(\text{CO}_3)_3(\text{aq})$	30.55 ^e
$\text{UO}_2^{2+} + 2\text{Cl}^- \rightleftharpoons \text{UO}_2\text{Cl}_2(\text{aq})$	-1.1
$\text{UO}_2^{2+} + \text{SO}_4^{2-} \rightleftharpoons \text{UO}_2\text{SO}_4(\text{aq})$	3.15
$\text{UO}_2^{2+} + 2\text{SO}_4^{2-} \rightleftharpoons \text{UO}_2(\text{SO}_4)_2^{2-}$	4.14
$\text{UO}_2^{2+} + \text{SiO}_2(\text{OH})_2^{2-} + \text{H}^+ \rightleftharpoons \text{UO}_2\text{SiO}(\text{OH})_3^+$	21.54 ^f

Uranium high chemical reactivity causes it to readily react with most elements. The tetravalent and hexavalent uranium often forms complexes with hydroxides, hydrated fluorides, and phosphates (Craft *et al.*, 2004). Table 1-2 illustrates the complexity of U reaction showing only some of the important reactions and their formation constants.

The speciation and its pH-dependency is exhibited by existence of either less or more soluble species in different pH regions. Under oxidizing alkaline conditions, species that are more soluble tend to exist, predominantly in form of carbonate, phosphate and hydroxyl complexes. Under near neutral pH conditions, hydroxide

complexes such as UO_2OH^+ , $(\text{UO}_2)_2(\text{OH})$, $(\text{UO}_2)_3(\text{OH})_7$ and phosphate complexes such as UO_2HPO_4 and $\text{UO}_2(\text{HPO}_4)_2^{2-}$ tend to form (Fomina *et al.*, 2007). At lower pH, the number of exchange sites becomes reduced on variable charged surfaces (e.g. natural organic matter (NOM) and iron- and aluminium-oxides) (Maity *et al.*, 2013) and U (hydr)oxides tend to predominate. The effect of pH on U speciation and sorption has been extensively studied (Catalano & Brown, 2005; Clark *et al.*, 2011; Krestou & Panias, 2004; Maity *et al.*, 2013; Uyu *et al.*, 2014) but remains a focus of U research due to a high level of importance and dearth of clear information in many areas.

Carbonate complexes are an important group of U species because of their high solubility and mobility. Soils exhibit higher CO_2 concentrations as compared to the atmosphere, typically containing 0.3-3 % CO_2 but can reach up to 10 % of the soil air at 1 m depth, under waterlogging, or in the vicinity of plant roots (Sposito, 2008). This disproportion with the atmospheric CO_2 partial pressure (P_{CO_2}) is due to biotic constituent of the soil. Consequently, carbonate ligands that originate from dissolved CO_2 tend to be abundant and may have significant impact on the soil solution chemistry.

Under alkaline pH and in the presence of dissolved CO_2 , U(VI)-carbonate complexes usually form and adsorption is insignificant (Davis *et al.*, 2002). The increased solubility can be explained by the competition of complexing carbonate ligands for available U(VI), which will reduce the aqueous activity of UO_2^{2+} and will drive the reaction in the direction of decreasing sorption (Pabalan *et al.*, 1998). In the absence of carbonates in soil, it is rather the surface complexation processes that control sorption of uranium cations (e.g., UO_2^{2+} , UO_2OH^+) (Abdelouas *et al.*, 2000). At the pH range 6-10, mainly soluble bicarbonate and tr carbonate species dominate (Maity *et al.*, 2013). Lee & Yun (2013) investigated the formation of ternary $\text{CaUO}_2(\text{CO}_3)_3^{2-}$ and $\text{Ca}_2\text{UO}_2(\text{CO}_3)_3(\text{aq})$ complexes under neutral to weakly alkaline conditions using fluorescence spectroscopy. They found that the presence of calcium ions, Ca^{2+} , was important in U species distribution. Formation of various carbonate Ca-UO₂²⁺-CO₃²⁻ complexes were found to be dependent on pH and Ca^{2+} concentration. This is important in soils, where both CO_3^{2-} and Ca^{2+} are typically abundant. The findings coincide with Fox *et al.*'s (2006) study, where it was concluded that Ca^{2+} presence can significantly impact U aqueous speciation and sorption. They observed almost doubled adsorption of

U(VI) on quartz when Ca^{2+} was added and complexed with U-carbonate species (at pH 7-8.75).

Natural organic ligands also tend to favour U(VI) dissolution as shown by numerous studies (e.g. Bednar *et al.*, 2007; Evans *et al.*, 2011). However, sorption enhancing the effect of NOM has also been reported (Niu *et al.*, 2009; Semião *et al.*, 2010). Humic and fulvic acids represent some of the most important metal complexing ligands in NOM. These acids were found to strongly bind U(VI), with humic complexes being slightly stronger than fulvic ones. The stability of such complexes was strongly pH-dependent (Lenhart *et al.*, 2000). The pH-dependency is the most likely explanation of the contradicting findings on U sorption in the presence of NOM. The NOMs consist of polyfunctional, polyelectrolytic, heterogenous organic molecules that possess different physicochemical properties (Lenhart & Honeyman, 2000). Although the number and strength of metal binding sites on NOM are highly variable, typically 90 % of the binding sites are the weaker sites. Lesher *et al.* (2013) used field-flow fractionation and Inductively coupled plasma mass spectrometry (ICP-MS) to compare U transport in systems with and without humic substances present; their study concluded that NOM presence enhanced transport and remobilized the U previously adsorbed. Additionally, Tinnacher *et al.* (2013) studied the effect of fulvic acid (FA) on U(VI) sorption kinetics to silica gel. They found FA significantly impacted U(VI) sorption as compared to FA ligand-free system. However, the shift in sorption rate was either slower or faster, depending on the mechanisms involved. The authors suggested possible underlying mechanisms behind the different sorption rates to be: dissociation of metal-ligand complex prior to the sorption of free metal, and competitive sorption (both leading to slowing sorption). The NOM sorption kinetics were also suggested to enhance or lower sorption rates.

Understanding and modelling of interactions between uranyl ion and FA in the environment should be included in U fate modelling because FA is one of the most abundant and reactive components of dissolved organic matter. Uranium can form various UO_2^{2+} -FA complexes according to functional groups present in FA molecular structure (Zhu *et al.*, 2014). The effect of pH plays an important role and generally binding of metal ions with humic substances (i.e. HA and FA) increases with pH

because the hydrogen ion acts as a competitor to the metal ion on functional groups such as carboxylic acid and phenolic groups (Zhu *et al.*, 2014).

Humics can also impact U bioreduction and oxidation in soil and groundwater, especially in presence of Ca^{2+} . Gu *et al* (2005) found that under anaerobic conditions, biological reduction of U(IV) was enhanced where humics were present in the system. The authors found HA to be more effective than FA. The effect was attributed to the ability of humics to facilitate electron-transfer reactions and/or complexation with Ca^{2+} and Ni^{2+} ions added to the system. The same research showed contrasting effect of the humics on U(IV) under aerobic conditions due to complexation of the humics with U and hence increasing U(IV) oxidation. The study indicates sensitivity of the effect of NOM on U speciation in response to pH and redox changes. Generally, introduction of FA strongly affects the shape of the U(VI) speciation and sorption pH dependence. In the systems containing FA, the sorption decreases with increasing pH due to formation of fairly stable U-fulvate complexes which are neutral or negatively charged and hence do not adsorb readily on the negatively charged surfaces (Kornilovich *et al.*, 2001).

The soluble U complexes may be fixed to the solid phase if active sorbents are present in the system, such as iron and manganese compounds. These compounds form reactive gels which react with UO_2^{2+} to form a precipitate. The sorption may be facilitated also by other metal oxides, aluminosilicates, and carbonates (depending on pH, U(VI) activity in solution and ion composition of the solid phase) (Vodyanitskii, 2011).

1.4.3.2 Chemical speciation modelling

Speciation diagrams allow the prediction of U speciation under varying U concentrations, ionic strengths, temperature, pH of aqueous solution and CO_2 pressure. Such approximation of environmental conditions based on thermodynamic databases has been done using a number of tools. For example, the Visual MINTEQ is frequently used (Cheng *et al.*, 2007; Contardi *et al.*, 2001; Fan *et al.*, 2014) and so is PHREEQC (Bachmaf & Merkel, 2011; Chang *et al.*, 2014; Delle, 2001; Vetterlein *et al.*, 2008). These speciation models mostly share the limitation of assuming equilibrium and hence ignore the kinetics of precipitation, redox reactions, and adsorption (Markich, 2002).

An example of the effect of pH and ionic strength on U species distribution is given in Figure 1-5, indicating U speciation changes according to U concentration and the dominance of various U-carbonate species at alkaline pHs (Krestou & Panias, 2004). The simplified soil system studied in this thesis avoided many of the commonly reported U reactions in soil, such as complexation with phosphate and sulphate inorganic ligands known to retard U mobility (Zhou & Gu, 2005; Cheng *et al.*, 2007; Solgy *et al.*, 2015) and with organic ligands having ambivalent effect on U sorption (Cumberland *et al.*, 2016). The study rather concentrated on the often dominant species in soils and sediments, free UO_2^{2+} , and hydroxyl- and carbonate- U species (Liu *et al.*, 2011; Cumberland *et al.*, 2016; Liu *et al.*, 2013), assuming the aqueous carbonate concentration to be in equilibrium with the CO_2 pressure of the system.

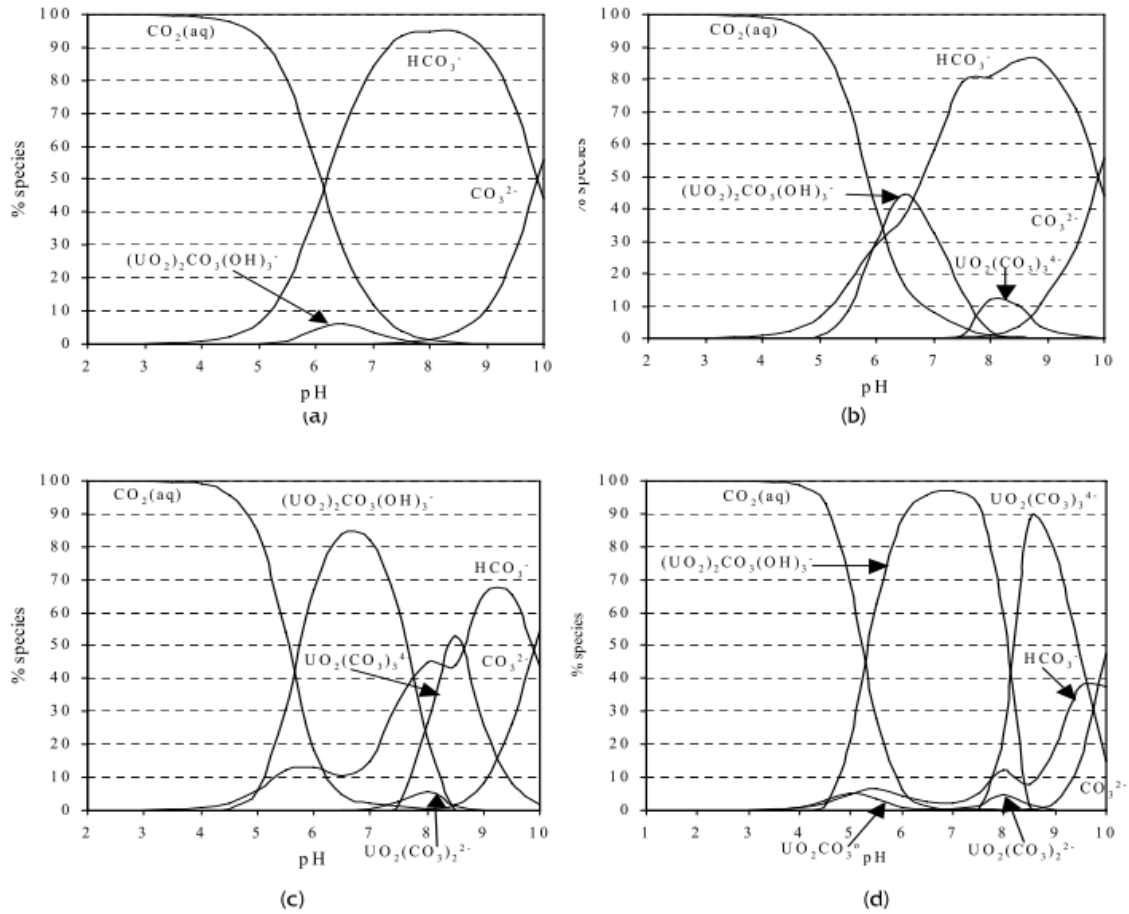


Figure 1-5 Uranium (VI) speciation diagram. Ionic strength = 0.1 M; T = 25°C. Total [U] = (a) 10^{-5} M , (b) 10^{-4} M , (c) 10^{-3} M , and (d) 10^{-2} M (Krestou & Panias, 2004).

1.4.4 Biotic controls of U speciation and transport

1.4.4.1 Plants and Uranium

Uranium soil and sediment contamination has two important aspects in relation to plants. Firstly, certain plant species are increasingly favoured in remediation of U contaminated sites due to lower costs compared to physical excavation and chemical methods (Rufyikiri *et al.*, 2006). Secondly, wild and crop plants can unintentionally take up U due to human activity and thus introduce U into the food chain (Anke *et al.*, 2009).

Uranium is not essential to plants, however it may be taken up accidentally with essential elements (especially when deficient in essential metals) (Viehweger & Geipel, 2010). Another purpose for U uptake is protection against U toxicity (exhibited as oxidative stress in plants) by its accumulation in less sensitive plant parts, usually in the root (Chen *et al.*, 2006; Shahandeh & Hossner, 2002; Thiry *et al.*, 2005). Moreover, the rate of uptake and distribution in different plant tissues is highly variable from species to species (Shahandeh & Hossner, 2002).

Certain plant species, such as sunflower (Shahandeh & Hossner, 2002), are more suitable for U phytoextraction due to their U uptake characteristics, biomass produced and ease of management of the U containing biomass. Gramss *et al.* (2004) examined ways of making U (and other heavy metals) more phytoavailable for Chinese cabbage (*Brassica chinensis* L.) but less leachable by addition of solutions containing either CaCl₂, NH₄Cl, casein, sucrose, citric acid, or rape extract. They observed highest U uptake by the plants from U contaminated soil treated with citric acid. The citric acid addition caused alkalisation of the soil and hence solubilisation of U and all other non-nutrients (Al, As, Cd, Pb and Ti) in spite of high content of calcium and magnesium. The authors also suggest possible chelating capacity of the acid. Citric acid has been the focus of many studies concerned with U phytoremediation (Crean *et al.*, 2013; Duquène *et al.*, 2009; Ebbs *et al.*, 1998; Huang *et al.*, 1998) but also in general studies of U solubility (Lenhart *et al.*, 2000; Redden *et al.*, 2001).

1.4.4.2 Mechanisms of uranium uptake by plants

Soil heavy metal contamination forced plants to develop efficient strategies to cope with phytotoxic elements, including non-nutrient heavy metals such as uranium. Without such mechanisms, plants could succumb to their ability to accumulate inorganic nutrients and non-nutrients, which could cause acute and chronic effects on plants grown on contaminated soil (Yadav, 2010).

Generally, the root system is the primary point of entry of metal ions in soil solution. Essential metal nutrients then enter plant cells along with non-nutrient heavy metal ions by either binding with oxygen-rich ligands such as carboxylic groups (e.g. K, Ca and Mg) or by binding with sulphur- and nitrogen- rich ligands such as amino acids (e.g. Hg, Pb and Au). For other metals (e.g. Cd, Cu and Zn), plants have intermediate preferences (Nieboer & Richardson, 1980). In addition, heavy metals may be absorbed due to foliar deposition.

Plants prevent cellular uptake of heavy metals through several intracellular strategies, such as stimulation of efflux pumping metals from cytosol, chelation of metals by organic acids or metallothioneins (Kotrba *et al.*, 2009). Compartmentalization into the vacuole is another successful strategy (Hall, 2002). Mycorrhizal symbiosis and exudation of organic compounds can help to tolerate heavy metals at extracellular level (Schutzendubel & Polle (2002).

Specific mechanisms of U uptake by plants are complex and poorly understood due to interactions between plants, bacteria, fungi and other chemical species in the rhizosphere. For example, Misson *et al.* (2009) studied U availability and translocation in plants (*A. thaliana*) as affected by availability of phosphate. The study showed that without phosphate addition, U uptake lead to increase in plant biomass at low U additions (2 μM). In contrast, at higher additions (50 and 500 μM), the plant growth was drastically decreased. Bioaccumulation of U decreased at presence of P due to $(\text{UO}_2)_3(\text{PO}_4)_2 \cdot 6\text{H}_2\text{O}$ precipitation. Microscopic observations showed that U and phosphate additions changed acquisition mechanisms by modifying phosphate influx capacities due to the induction of high affinity phosphate transporters in phosphate-starved plants. Phosphate uptake was drastically reduced in presence of higher U

concentrations. This was attributed to functional expression of PHT1;4 gene, which is the most phosphate-regulated high affinity phosphate transporter gene in plants. Furthermore, nanoSIMS and TEM-EDX techniques revealed that U was accumulated preferentially in the external root cell layers, in cell walls, where they caused cellular damage. Some intracellular spots were also observed. Importantly, co-localisation of P and U in these intracellular spots indicates similar uptake mechanisms for P and U. Furthermore, the images identified U aggregation in small vacuoles inside the undifferentiated cells where U precipitated with Ca and P (Misson *et al.*, 2009).

Mihalík *et al.* (2012) studied citrate assisted phytoextraction of U by sunflowers grown in rhizoplan device containing soil layer and nutrient solution. They found that the flux of nutrient elements (Fe and Zn) affected U transfer to plants and its further distribution. The authors suggested that increase in translocation from root-to-shoot of both U and Fe was caused by U interference with mechanisms regulating Fe homeostasis. Citrate addition further enhanced U accumulation by plants and its translocation to shoots by mobilisation of U as U-citrate complexes. However, the mechanisms of translocation remained unknown. Mihalík *et al.* (2012) suggested that U forms may use the apoplastic or symplastic pathway to move inside the root up to the endodermis where, if the barrier is fully developed, they follow symplastic pathway. In contrast, if the endodermis barrier is not fully developed (e.g. at the root apex or where physical damage occurred), U is translocated by the passage cells and so does not have to be internalised to reach the xylem. Citrate (and other chelating agents) are known to change preferential pathways for metal uptake from symplastic to apoplastic at least partially as a result of physical damage caused by high concentration of complexant on root structure (Degryse *et al.*, 2006). Furthermore, the citrate complexation may exhibit concentration and kinetic dependence (Mihalík *et al.*, 2012) further indicating the complexity of U plant uptake.

1.4.4.3 Uranium in the rhizosphere

Uranium speciation and sorption in single mineral phases, sterilised soils and plant-free substrates will naturally differ from rhizosphere-relevant conditions. In the rhizosphere, in addition to abiotic control mechanisms of U transport, biotic processes may have

significant impact on U behaviour (Abdelouas *et al.*, 2000; Dupré de Boulois *et al.*, 2008). These biotic controls include soil-U-plant interactions, bioturbation and fungal and bacterial activity. Figure 1-6 gives a schematic description of the major processes in the rhizosphere (Luster & Brunner, 2006). The effects of root induced changes in soil pH and CO_2 pressure are particularly important for soil U solubility and hence bioavailability to roots.

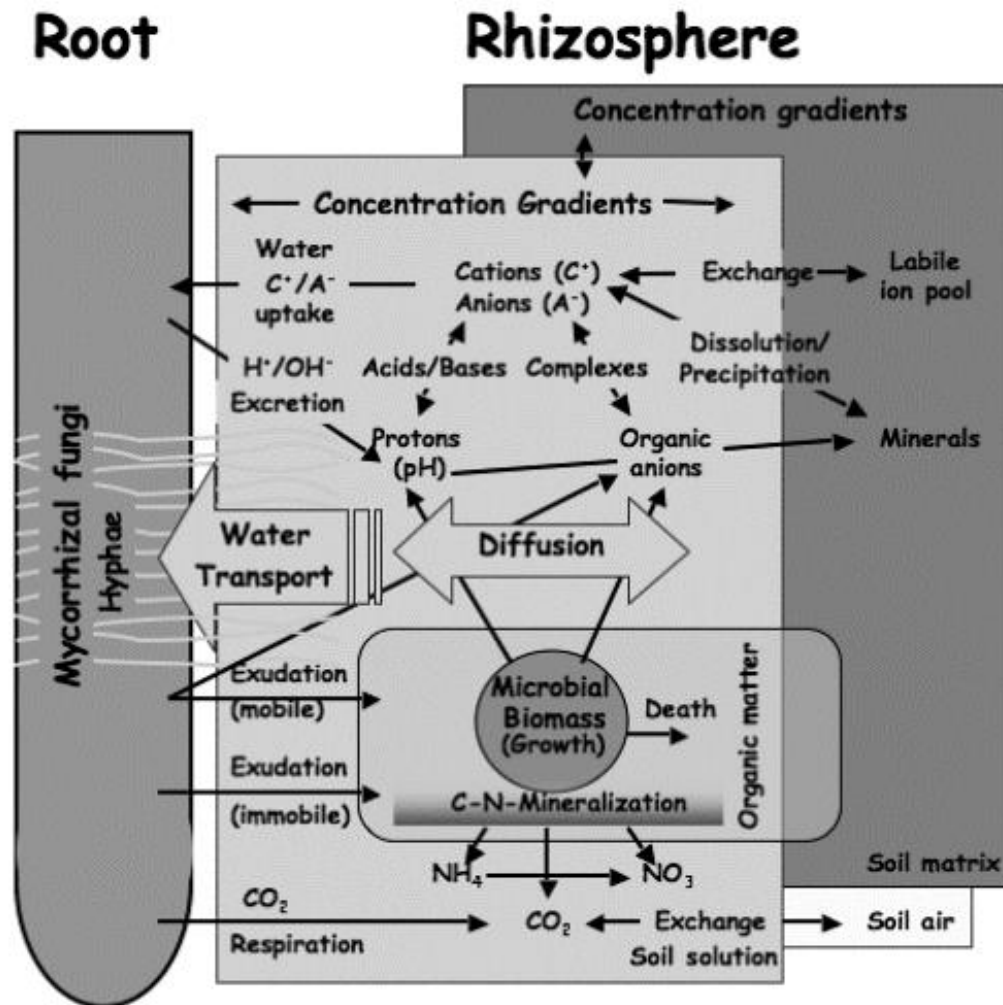
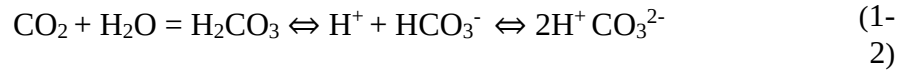


Figure 1-6 Schematic representation of major processes occurring in the rhizosphere (Luster & Brunner, 2006).

In the absence of plants and other organisms, soil CO_2 will reach equilibrium with the atmosphere (Rowell, 1994). However, plants and soil biota alter the equilibrium by producing CO_2 faster than it can diffuse out of the soil through the soil air, so the CO_2

pressure in soil air in the root zone is generally far greater than that in the atmosphere (Tinker and Nye, 2000). For example, Blossfeld *et al.* (2013) used planar optodes to monitor CO₂ dynamics in the rhizosphere of *Viminaria juncea* roots and showed strong impact of a single growing root on the local CO₂ pressure over several millimetres within the soil, reaching values of up to 70% vol. %. Soil respiration is the second largest flux of carbon in most terrestrial ecosystems. However, microbial soil respiration and root CO₂ production are difficult to distinguish reliably (Hao & Jiang, 2014; Usselman *et al.*, 2000).

Some of the CO₂ in the soil air dissolves in the soil solution and forms HCO₃⁻ and CO₃²⁻, depending on the pH:



Plants also alter the rhizosphere pH in response to their intake of nutrient cations and anions. Because there must be electrical neutrality across the root-soil interface, the root will balance the intake of nutrient cations (NH₄⁺, Ca²⁺, Mg²⁺, K⁺) over anions (NO₃⁻, H₂PO₄⁻, SO₄⁻, Cl⁻) by excretion of hydrogen (H⁺) or bicarbonate (HCO₃⁻) ions (Kirk *et al.*, 2014).

The pH change in the rhizosphere resulting from the release of the H⁺ or HCO₃⁻ by the root is propagated away by the diffusion of mobile acid-base pairs in the soil. Acids move from low pH to high and bases in the opposite direction. The main acid-base pairs are HCO₃⁻ - H₂O and H₂CO₃^{*} - HCO₃⁻ (Tinker & Nye, 2000).

Various organic compounds produced by plants facilitate access to nutrients and their uptake. These include acid anions (e.g. malate, citrate, oxalate, etc.) and siderophores (metal chelating molecules produced by roots and fungi and bacteria associated with plant root) (Duquène *et al.*, 2006). These solubilising agents may play an important role in potential U mobilisation from bulk soil to depleted zone for root uptake.

Plant association with mycorrhizal fungi can further alter U mobility and translocation in the soil and its uptake by plants (Chen *et al.*, 2006). The plant-fungi

association is well-documented to help protect plants from toxicity of non-essential heavy metals by promoting metal retention in the roots (Chen *et al.*, 2006; Rufyikiri *et al.*, 2006) or in the mycelia of the fungi (Rufyikiri *et al.*, 2002; Rufyikiri *et al.*, 2004; Rufyikiri *et al.*, 2003). However, these studies are limited as they were carried out predominantly under laboratory conditions and on single plant species. Davies *et al.* (2018) studied four plant species and their arbuscular mycorrhizal (AM) fungi associations in field conditions in two uranium, thorium and radium contaminated sites. They observed no significant correlation between abundance of AM fungi and U transfer into the roots of the field samples. The primary role of the fungi is phosphate uptake facilitation, which has similar uptake root to U, but each AM fungi species has different capabilities of such facilitation, therefore questioning the general assumptions about the AM fungi role in field conditions (Davies *et al.*, 2018).

1.4.4.4 Other biotic factors affecting uranium transport

Uranium transport may be further affected by biotic processes such as bioturbation by earthworms and macro-invertebrae (Lloyd *et al.*, 2009). However, it is fungi and microbial communities that should be considered on a root-uptake scale. Microbes play a complex and important role in the biogeochemistry of metals, including U. Solubilisation of U from minerals by microbial processes can increase its bioavailability, while other processes, such as microbial bioreduction of U(VI) to U(IV), can immobilize U and therefore reduce its bioavailability (Gadd, 2007). Microbial metabolism produces a wide array of organic ligands (e.g., siderophores, carboxylic acids, etc.) available for U complexation (Tinker & Nye, 2000).

Microbes are increasingly used in soil, sediment and water bioremediation of U (Chang *et al.*, 2014; Ray *et al.*, 2011; Sheng & Fein, 2014). Uranium reduction from hexavalent (soluble) to tetravalent (sparsely soluble) is one of the key mechanisms (Ray *et al.*, 2011). Abdelouas *et al.* (2000) compared bacterial reduction of U in groundwaters with different chemical composition. The species responsible for U reduction in the study were primarily sulphate-reducers. Addition of nutrients was found to further stimulate U reduction although with sufficient amounts of iron sulphate necessary to prevent reoxidation of U in oxygenated waters. Dong *et al.* (2006)

examined the role of microorganisms (in addition to physical mechanisms) in the fate of U(VI) in sediment from Chesapeake Bay, USA. The site was used for testing military ammunition containing DU which led to deposition of > 70 000 kg of DU to local soils and sediments. The authors found that sorption and biotransformation of U(VI) decreased U solubility via rapid association of U(VI) with NOM (i.e. via adsorption) followed by slow bioreduction of U(VI) to U(IV) by bacteria of the order *Clostridiales*. The bioreduction of U must be determined from analysis of particle-associated U because U(IV) is extremely difficult to detect by monitoring U concentration in solution due to its insolubility. Natural U isotopes are all radioactive while DU, which is the removed fraction of U after the ^{235}U enriched fraction is produced, has only trace of decay products after ^{234}Th and hence has only low activity. Never the less, there is radiological hazard connected with DU inhalation of aerosols and soil ingestion. Such internal exposure to alpha radiation, however limited, may be accompanied by external irradiation due to beta and gamma rays emitted by DU (IAEA, 2010).

Interaction of certain U species with organic acids produced by symbiotic and free-living fungi can lead to U biotransformation (Gadd & Fomina, 2011). Fomina *et al.* (2007) examined the ability of saprophytic, ericoid and ectomycorrhizal fungi to transform uranium oxides UO_3 and U_3O_8 . They used advanced solid state speciation and scanning electron microscopy (SEM) to locate and identify U forms in the samples. They found that fungi exhibit high uranium oxide tolerance, capacity to solubilize these oxides and can accumulate U in their mycelium to over 80 mg g^{-1} dry weight biomass. There are several mechanism of solubilisation of U by fungi, including protonation (acidification), chelation (complexation), and bioaccumulation, with complexation being the more effective process (Gadd, 2007). For example, addition of citrate in U contaminated soil increased U uptake by beet as a result of lowering soil pH and hence changing U speciation, making it more phytoavailable. The soil acidification was induced either by HEDTA or citric acid soil amendments, however HEDTA had no effect on soil pH nor U solubility. In contrast, citric acid lowered soil pH to pH 5.0 and stimulated U shoot accumulation by beet, showing that uranyl cation was the most readily phytoavailable U species for beet (Ebbs *et al.*, 1998). However, the authors point out that soil amendment with citric acid may lead to formation of U-citrate

complexes which may be altered by microbial action and photodegradation, forming insoluble, non-leachable complexes such as uranium trioxide. Formation of such complexes is not desirable in soil phytoremediation but could be favourable in U recovery from aqueous systems (Ebbs *et al.*, 1998). In a study by Fomina *et al.* (2007), oxalic acid was found to be an important compound in uranyl oxide complexation by oxalate. Most of the uranium within the fungal biomass was identified by x-ray absorption spectroscopy as uranyl ion coordinated to phosphate ligands. In ectomycorrhizal fungi, mix of phosphate and carboxylate coordination was found.

Because soil biology might affect radionuclide behaviour, soil samples are frequently sterilised (Chen *et al.*, 2008; Davies *et al.*, 2015; Helgason *et al.*, 2002; Rufyikiri *et al.*, 2004). Various methods of sterilisation exist (e.g., autoclaving, gamma irradiation, chemical sterilization, etc.). However, the review of available methods and their impact on physio-chemical soil properties showed that the trade-off for microbial inhibition may be limiting (Trevors, 1996; Wainwright *et al.*, 1980), depending on the purpose of the study. Although all the above methods eliminate the microbiological component of the soil, it might be preferable to maintain some communities in order to preserve the characteristics of the soil. Furthermore, none of the methods would guarantee sterile soil for longer experiments (> 3 weeks) (Brito *et al.*, 2009; Fraser *et al.*, 2016).

However, it can be assumed that the AM fungi and their spores are highly reduced by the soil sieving and grinding because any form of structural disturbance has the potential to be as effective as some of the mentioned sterilization methods without the release of nutrients and other undesired side effects (Brito *et al.*, 2009). This assumption can be supported by a spore count under a microscope. Nevertheless, the soil in this study remained unsterilized in order to prevent any changes in soil chemistry resulting from its sterilisation and also to maintain the microbial aspect of U-soil interaction.

1.4.4.5 Methods of assessment of U phytoavailability

It is generally accepted, that only dissolved U species are bioavailable. However, there are differences between uptake of various dissolved U species. It is mainly free UO_2^{2+} , and uranyl-phosphate and uranyl-carbonate complexes that are considered more likely

to be taken up by plants (Gramss *et al.*, 2004). However, U solubility remains the main indicator of potential phytoavailability.

Uranium solubilisation is most commonly assessed by sequential extraction (Lloyd *et al.*, 2009; Schultz *et al.*, 1998; Suresh *et al.*, 2014; Viehweger & Geipel, 2010) which separates total U in the soil into dissolved, readily soluble, less soluble, poorly soluble, and residual (insoluble) fractions. Various sequential extraction methods for heavy metals exist (a comprehensive review is given by Filgueiras *et al.* (2002)). The most popular and accepted is the Community Bureau of Reference (BCR) sequential extraction method based on the method developed by Tessier *et al.* (1979). Comparison of other sequential extraction methods is available from Kennedy *et al.* (1997), Oyeyiola *et al.* (2011) and Vandenhove *et al.* (2014).

The majority of sequential extraction methods are time consuming and results are sensitive to seasonal and site variability (Kennedy *et al.*, 1997). In addition, each extraction step can interfere with U and sorbent chemistry, affecting results in the following steps. Dissolution of organic matter and mineral phases may be another undesired effect (Thiry *et al.*, 2005). Therefore, the assessment of potential solubility may give inaccurate results. Another challenge with sequential extraction is the lack of standardisation and validation of the methods. This makes existing generic models unreliable as the methodologies are both site- and plant-specific (Thiry *et al.*, 2005).

To avoid some of the sequential extraction problems, single extraction (e.g. with CaCl_2 , NH_4NO_3 , NaNO_3 , etc.) and other methods are used to estimate metal bioavailability. The choice of the suitable extractant is crucial and has to match the solute studied and the purpose of the study. Each of these methods has its limitations and suffers from low rates of repeatability as their execution varies from laboratory to laboratory. Standard reference materials are lacking, making results comparison unreliable. Kennedy *et al.* (1997) published an exhaustive critical review of extraction methods for assessment of radionuclide and heavy metal availability for root uptake.

Background electrolyte concentration can significantly affect sorption to permanent-charge sorption sites; the higher the concentration, the greater displacement of the exchangeable cations into solution and hence the metal concentration in solution

increases. In addition, the variable-charge surfaces will become increasingly more negative with increase of the background electrolyte. The displacement of protons from variable-charge sites into the solution can then lower the pH with increasing background electrolyte concentration (Molina Millán *et al.*, 2006; Sposito, 2008).

Many researchers prefer the use of 0.01 M CaCl₂ as a good universal extractant and background electrolyte because it has similar ionic strength as the typical salt concentration in soil solutions (0.03 M) (Houba *et al.*, 2000). Therefore, the adsorbed ions should be only slightly disturbed by exposure to 0.01 M CaCl₂ (Tinker & Nye, 2000). The CaCl₂ solution is well suited for measurements of UO₂²⁺ bioavailability and sorption due to the bivalent nature of the calcium cation (Ca²⁺). The Ca²⁺ is the typical dominant cation in soils, but depending on the soil pH and soil parent material it can be also Al³⁺ (acidic soils), Na⁺ (sodic soil), or Mg²⁺ (e.g., serpentine) (Molina Millán *et al.*, 2006). In addition, Ca²⁺ is the primary cation of the adsorption complex of soils and hence the CaCl₂ solution is capable of more efficient extraction of cations at lower salt concentrations than extractants based on monovalent cations (Houba *et al.*, 2000). The chloride anion (Cl⁻) is a metal (M⁺) complexing agent and therefore can extract (i.e. desorb) metal cations according to the strength of complexes of the metal of interest and other metal complexes (Molina Millán *et al.*, 2006). Houba *et al.* (2000) provides a good summary of the preferential use of 0.01 M CaCl₂.

In spite of the complications in measuring bioavailable U by single and sequential extraction methods, these methods can provide useful information of U association with specific soil components. However, they provide only a relative empirical method to study U phytoavailability.

An alternative approach to chemical extraction is to deploy diffusive gradient in thin films (DGT) devices, which are designed to measure the bioavailable fraction of a metal by capturing its bioavailable mass in a metal-specific resin. Vandenhove *et al.* (2007c) compared the DGT method with U in soil pore water, and U measured by several single extraction methods to predict U phytoavailability in soil. No correlation was found for pore water concentrations and U selective extractions. In contrast, the team observed high correlation of DGT measurements with measured U uptake by ryegrass. However,

the calculation of the DGT measured concentration (C_{DGT}) was found sensitive to the input value of diffusion coefficient, which is often taken from the literature. In another study, Vandenhove (2007a) did not observed satisfactory explanation of the U spiked soils and DGT measured U uptake by ryegrass. Vandenhove concluded that DGT is not a suitable method to assess U.

A more realistic approach to study U phytoavailability in soil is by setting up a mesocosm that would measure direct uptake of U by plants under controlled conditions. An example of such method is use of rhizobox (soil compartments are separated by a cloth, physiochemical properties of the soils measured before and after diffusion into plant occurs, and plants are analysed after a certain period for U content) (Davies *et al.*, 2015; Youssef & Chino, 1989). Another more realistic approach found was the measurement of DU in plant-soil microcosm (*Lupinus albus*) where soil solutions were sampled and analysed using single-cell sampling-and-analysis (SiCSA) and capillary electrophoresis. The aim of the study was to understand the effect of root exudates (citrate, malate) on DU solubility, which was found to be significant (Tandy *et al.*, 2013). However, these studies are complex and time consuming. In addition, the information is again species- and soil- specific and limited in terms of transferability to other soil systems.

Considering the limitations of the above methods and of soil-to-plant transfer (factors discussed next), it becomes evident that the models based on the parameters obtained from these methods may not be realistic. Therefore, validated total chemical extraction combined with robust method of data analysis may offer a more reliable solution to assess potential U phytoavailability. Total extraction by digestion in concentrated acids facilitated by heat and sometimes pressure (e.g. aqua regia method) combined with state-of-the-art instrumentation such as ICP-MS generally deliver very good recovery of U (Crean *et al.*, 2013; Sansone *et al.*, 2001; Sims *et al.*, 2008). Most importantly, the experimental design for evaluation of U phytoavailability should consider not only U in bulk soil but also its diffusion and reaction on the root-relevant scale.

The importance of the effect of plant activity on soil chemistry and hence U speciation and mobility is usually ignored in empirical models of U uptake by plants. These models mostly use simple transfer factors (TF), i.e. soil-to-plant transfer ratio. For example, Chen *et al.* (2006) studied arsenic and uranium accumulation by Chinese brake fern (*Pteris vittata* L.) with or without inoculation with AM fungi (*G. mosseae* or *G. intraradices*). The results showed a significant increase of U concentration in the root in AMF inoculated plants. However, the study concentrated on biological aspects and soil physical and chemical properties were largely neglected.

The lack of connection between TF and soil properties was shown by a review of Vandenhove *et al.* (2009) which showed that a striking 50% of the reviewed studies ignored the importance of soil properties. This was the case elsewhere (e.g. Nyade *et al.*, 2013; Viehweger & Geipel, 2010). The evidence of the role of soil chemistry in U speciation and hence mobility is unquestionable (Davies *et al.*, 2018; EPA, 1999).

Attempts to encompass both soil and plant influences involved in U transport and uptake exist (Shahandeh & Hossner, 2002; Thiry *et al.*, 2005). However, they remain empirical and ignore the reaction rates and the mechanisms behind the U transfer to and into the plant root. Therefore, more sophisticated models that consider both U transport and plant uptake mechanisms are essential to correctly and accurately assess potential U phytoavailability.

1.4.5 Transport and reaction processes in soils

1.4.5.1 Diffusion theory

Solute movement in soils occurs by convection and diffusion. Diffusion is the governing process where solute concentrations in soil solution are small enough, as is often the case for strongly sorbing contaminants. Diffusion occurs in all phases: gas, liquid and solid. Therefore diffusion of solute takes place in air-filled pores, the pore solution and by surface diffusion.

In soil studies, diffusion in all phases is relevant, however, for non-volatile solutes it is the liquid phase and solid phase that are of most interest. An ion has to travel through the interconnected and dead-end web of pores with varying soil solution content

affecting its mobility. The diffusion through the soil pore network is accompanied by interchange with the solid surfaces. Most ions are relatively immobile in the soil solid. Furthermore, changing environmental conditions (such as temperature, pH and redox) may cause desorption from the soil solids and alter the diffusion rate due to movement on solid surfaces. Nevertheless, diffusion in solution is of paramount importance in plant root uptake of nutrients and other substances.

Theory

The theory of solute diffusion in soils is well established (Tinker & Nye, 2000). The basis is that, for a solute with concentration gradient $\partial C / \partial x$ across a section of soil, the flux, F , ($\text{mol m}^{-2} \text{s}^{-1}$) of the solute across the section is given by Fick's first law

$$F = -D \frac{\partial C}{\partial x} \quad (1-3)$$

where D ($\text{m}^2 \text{s}^{-1}$) is the diffusion coefficient of the solute in the soil. The flux is the sum of the flux in liquid and soil phases through the solid portion of the cross-section:

$$F = F_L + F_S \quad (1-4)$$

where the subscript $_L$ and $_S$ stand for liquid and solid phase.

The diffusion coefficient is given by

$$D = D_L \theta f_L \frac{dC_L}{dC} + D_S \rho f_S \frac{dC_S}{dC} \quad (1-5)$$

where D_L ($\text{m}^2 \text{s}^{-1}$) is diffusion coefficient in free solution, θ ($\text{dm}^3 \text{dm}^{-3}$) is the soil volumetric water content, f_L (dimensionless) is an impedance factor for the tortuosity of the liquid phase diffusion pathway, and the derivative dC_L/dC gives the relation between the whole soil concentration of the solute and the concentration in the soil solution. The term for solid phase includes: D_S is surface diffusion coefficient, ρ (kg dm^{-3}) is soil bulk density, f_S is the impedance factor for solid phase, and dC_S/dC is the solute concentration on the solid (Nye, 1966).

The D coefficient is a function of the soil water content and decreases with decreasing water content (Miyasaka *et al.*, 2014). Surface diffusion is often unimportant for strongly sorbing solutes (as observed for phosphorus by Nye already in 1966 and by Rowell *et al.* in 1967). Radionuclide surface diffusion is significant only in high activity clays compacted at high dry densities and is U species-dependent (Shackelford & Moore, 2012).

If surface diffusion is unimportant

$$D = D_L \theta f_L \frac{dC_L}{dC} \quad (1-6)$$

The value of D (in $\text{m}^2 \text{s}^{-1}$) indicates the overall rate of diffusion which comprises diffusion coefficient of all individual species of the solute. The rate of change in the concentration of the diffusing solute at any point along the concentration gradient is given by Fick's second law:

$$\frac{\partial C}{\partial t} = \frac{\partial}{\partial x} \left(D \frac{\partial C}{\partial x} \right) \quad (1-7)$$

The soil is a complex media with many biogeochemical processes taking place. These processes may further affect the solute concentration in the soil volume at a distance travelled, ∂x . If the solute undergoes reactions that are slow compared to diffusion, then

$$\frac{\partial C}{\partial t} = \frac{\partial}{\partial x} \left(D \frac{\partial C}{\partial x} \right) - R \quad (1-8)$$

where R is the rate of reaction. The R term can have positive and negative value, depending on whether the solute was added (R is positive, i.e. it is the excess flux resulting from any solute mobility on the solid) or removed (R is negative, i.e. immobilised) into the soil volume by these processes. Each process can be individually added under its own R term (Kirk, 2004).

The rate of diffusion will depend on many factors such as root uptake, microbial activity, pH changes, soil structure, texture, moisture content, tortuosity, and

composition (i.e. will differ in each soil) (Tinker & Nye, 2000). The diffusion coefficient enables us to predict the extent of the solute movement accounting for all the soil and solute characteristics and interactions. All the important diffusion mechanisms in the soil-root system are elucidated in Figure 1-7.

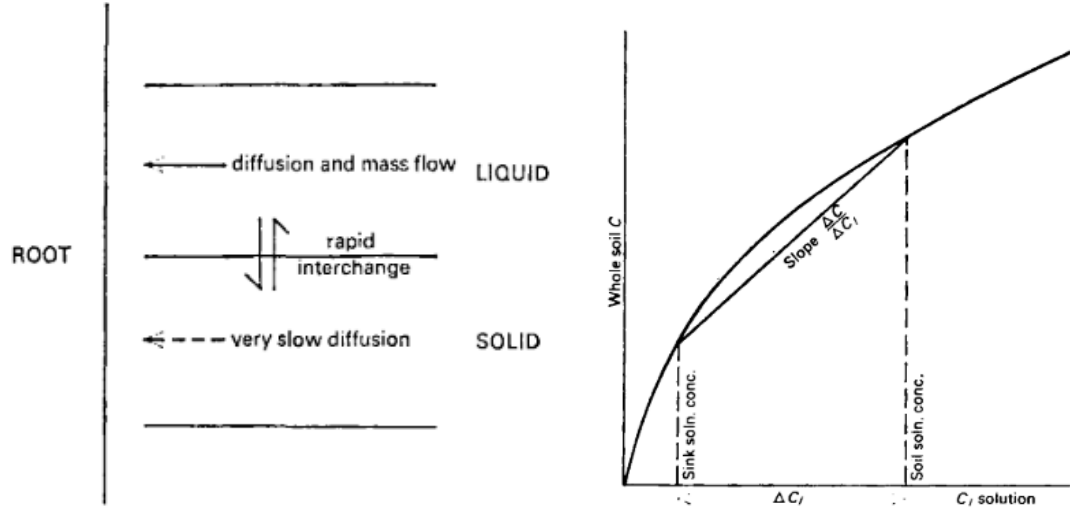


Figure 1-7 Approximate expression of the diffusion coefficient in soil Equation 1-5 (left), and of the soil-solution concentration profile near the root (right) (Nye, 1968).

If D is constant, the distance travelled, x (in m), by a solute is calculated from the square root of diffusion duration:

$$x = \sqrt{Dt} \quad (1-9)$$

The diffusion rate then describes how rapidly the diffusion distance advances with time ($\partial C/\partial t$). The diffusivity increases with temperature according to Arrhenius equation:

$$D = D_0 e^{-E/RT} \quad (1-10)$$

where T is the absolute temperature ($^{\circ}\text{K}$), D_0 ($\text{m}^2 \text{s}^{-1}$) is value of D at $T = \infty$, E is the activation energy ($\text{kJ mol}^{-1} \text{K}^{-1}$), and R is the universal gas constant (J mol^{-1}) (Crank *et al.*, 1981).

There are many types of diffusion described for environmental systems. The terminology in literature is, however, often confusing as the same phenomena are given different names by different authors. Zhang (2010) provides a good overview of various kinds of diffusion encountered in nature and experimental studies. To name a

few, self-diffusion represents diffusion where no chemical potential gradient exists and diffusion is monitored through difference in isotopic fraction (or by using an isotopologues, such as Cl^- and Br^-). Tracer diffusion describes detection of concentration gradient of a (radio)tracer in otherwise uniform bulk composition. The diffusivity is then a constant (i.e. concentration-independent) at low concentrations (Zhang, 2010). In contrast, bulk diffusion describes diffusion of multispecies diffusion in a soil where various solutes co-exist and may interact between themselves and with the species of the diffusing solute of interest. Transport of the array of U species in soil to plant roots is therefore not a subject to self-diffusion but bulk-diffusion (Nye, 1966).

Unless C_L is proportional to C_S (usually not the case), for the ions participating in bulk diffusion

$$\frac{dC_L}{dC} \neq \frac{C_L}{C} \quad (1-11)$$

and

$$\frac{dC_S}{dC} \neq \frac{C_S}{C} \quad (1-12)$$

However, under assumption that ions in solution and those in solid phase remain in equilibrium on entering a new zone, then dC_L/dC and dC_S/dC in Equation (1-5) may be deduced from $\partial C_S/\partial C_L$ which is the slope of the adsorption isotherms at a given concentration. The slope depends on all ions present in the system and therefore the system conditions during the isotherm determination must match the studied soil conditions (Nye, 1966).

Translated in terms of electro-neutrality, all ions have to travel in such arrangement to maintain the electro-neutrality of the overall soil. This creates an electric potential between the ions diffusing together and consequently the slower ion causes the faster one to slow down and vice versa. As a result, the flux of the ion of interest comprises of a diffusion gradient arising from its own properties as well as the gradient of the diffusion potential due to interaction with other ions of different potentials (Kirk, 2004).

The theory above is mathematically expressed by the Nerst-Planck equation along the x-axis:

$$F_{LA} = -D_{LA} \left(\frac{\partial C_{LA}}{\partial x} + \frac{Z_A C_{LA} F'}{RT} \right) \frac{\partial \psi}{\partial x} \quad (1-13)$$

where F' is the Faraday constant ($J \text{ mol}^{-1} \text{ V}^{-1}$), Z_A is the charge of the ion A and ψ is the potential.

The potential term can be ignored where the ion A concentration is negligible. In such cases, the concentration gradient is the driving force of the diffusion. This will not be true where ionic strength of the species contributes significantly towards the total ionic strength of the system.

If there is no net flux of charge then $\sum Z_i F_{Li} = 0$ (Vinograd & McBain, 1941), where i represents the ionic species of charge Z and flux in liquid phase F_{Li} .

Substituting the potential/distance term, $d\psi/dx$, with the ionic concentration gradient gives equation:

$$F_{LA} = -D_{LA} \frac{\partial C_{LA}}{\partial x} + Z_A C_{LA} D_{LA} \frac{\sum D_{Li} \partial C_{Li} / \partial x}{\sum Z_i^2 D_{Li} C_{Li}} \quad (1-14)$$

The ion can be present in the system as a free ion or in a complexed form combined with various ligands. The complexed forms show smaller diffusion mobility (Kirk, 2004). A comprehensive summary of mathematics of diffusion is given by Crank (1975).

1.4.6 Measurement of uranium diffusion and reaction in soil

1.4.6.1 Effect of soil physical properties on U transport

Mobility of U in soils will be altered by any soil property that alters the sorption mechanisms. Sorption is the main diffusion-limiting process and so quantification of sorption is essential in diffusion coefficient calculations. Soil physical properties such as soil texture and structure, organic carbon content (OC), cation exchange capacity (CEC), moisture content and bulk density all affect solute diffusion in a given soil.

For example, since adsorption occurs on solid surfaces, surface area would be expected to influence sorption characteristics. Payne *et al.* (2011) assessed normalisation of distribution coefficient (K_D) values against surface area according to $K_a = K_D/SSA$, where K_a is the surface area normalised K_D value (distribution coefficient), and SSA is specific surface area. They found the approach to be a good method for harmonisation of K_D for U sorption models but with a significant limitation of the concept at trace U concentrations.

Vandenhove *et al.* (2007b) found a linear relationship between ^{226}Ra sorption and CEC and OC. The linear increase of sorption with increase in OC was found also for U by Maity *et al.* (2013). There are numerous studies of the relation between U sorption and soil properties available (Bednar *et al.*, 2007; Catalano & Brown, 2005; Crançon & Van Der Lee, 2003; Fox *et al.*, 2006; Michard *et al.*, 1996; Pabalan *et al.*, 1998; Prikryl *et al.*, 2001).

Soil pore network geometry and connectivity affects the time a solute needs to access solid sorption sites. The rate of diffusion of an ion in soil can be altered due to tortuosity of the pathway the solute has to undertake to cross a section of soil through the pore system. Theoretical diffusion coefficient of an ion would be greater if tortuosity was omitted. However, particles and water occupy some of the pore network, and the molecules have to take a tortuous pathway, which impedes their progress (Rowell, 1994). The more tortuous the pathway, the greater the path length and the lower the concentration gradient along the path will occur (Tinker & Nye 2000). This tortuosity is accounted for in diffusion equation (1-6) by the term of impedance factor, f . The f -value is specific to each soil at given moisture content and bulk density. The f -value is determined experimentally by measurement of self-diffusion of a non-sorbing solute by the method developed by (Pinner & Nye, 1982). Alternatively, the soil tortuosity is accounted for by the term of tortuosity factor (Moldrup *et al.*, 2001). There are various models for tortuosity factor mathematical determination (Bhadoria *et al.*, 1990). Chou *et al.* (2012) provides evaluation of a number of the models for variously saturated soils.

1.4.6.2 Measurement of reaction equilibrium and reaction kinetics

There are various methods of measurement of reaction either at equilibrium (i.e. when adsorption rate equals desorption rate) and of kinetically controlled reactions. The most frequently used methods include the batch method, the flow through method, the stirred flow-through reactor and zero-length column (Limousin *et al.*, 2007).

Each method is more appropriate for different ends. For example, the flow-through method allows to study sorption kinetics at realistic soil-to-solution ratio but the minimum mixing may neglect reaction on less accessible sites (Sparks, 1999), which is important in unsaturated soils. Other issues of the method application are summarised in the review of sorption isotherm by Limousin *et al.* (2007).

In contrast, the stir-flow reactor has a continuous flow of solution through the solid, which is stirred to ensure exposure of all solid particles to solution. The concentration of the solute of interest is measured in the effluent to determine sorption characteristics under given conditions (Sparks, 1999). For example, Liu *et al.* (2009) applied this technique to investigate the kinetics of U(VI) desorption from contaminated sediments from U.S. Department of Energy Hanford Site, Washington, USA. Three solutions of varying pH and calcium and carbonate concentrations were applied and reaction rates were measured. The results showed that the solution chemical composition led to sorption disequilibrium with faster desorption than adsorption rate. The results were used to test a multirate surface complexation model (SCM) for description of U(VI) desorption behaviour; the model fitted reasonably well. However, the method is sensitive to clogging by clay particles. The estimation of sorption (working with selenite) has been shown to be sensitive to flowing conditions and an alternative approach was suggested (Garcia-Sanchez *et al.*, 2014). Other criticism of the method are provided by Limousin *et al.* (2007).

The batch method is the most widely used method to study sorption at equilibria and also sorption kinetics. Shaken suspension method is the simplest form of a batch system based on shaking of vessels (such as centrifuge tubes) containing dispersed soil. Uranium soil-solution partitioning (i.e. sorption) has been studied extensively in shaken suspensions, especially in relation to nuclear industry and waste disposal (Ball, 2009;

Maity *et al.*, 2013; Missana *et al.*, 2004) but the method has been used also for predicting metal uptake by plant roots (Kirk & Staunton, 1989). The results are often expressed in the form of distribution coefficient (K_D) (Kaplan *et al.*, 2001; Payne *et al.*, 2011; Phillippi *et al.*, 2007; Shang *et al.*, 2011) and various sorption isotherms. One significant challenge of this method is the equilibrium state assumption.

Another disadvantage of the equilibria sorption parameters from shaken suspensions is that no information is obtained on reaction rates and on process mechanisms. In addition, shaking the soil may be too timely to register the completion of fast reactions. Too vigorous mixing may physically alter the solid surfaces (by abrasion); too little mixing may favour mass transfer and transport processes. Also, reverse reactions are not controlled (Sparks, 1999).

Nevertheless, equilibrium studies provide valuable information on the final state of the reaction. The K_D values are simple means of comparison of sorption behaviour of the same solute under changing system conditions and between different systems (under the same conditions) (Sparks, 1999). For these reason, the shaken suspension studies remain popular, even in recent times.

However, the K_D comparison between different studies is rarely possible, as different experimental conditions are employed and the information on soil-solution interchange only applies to the solute in the studied system under given conditions. The fact that K_D often varies with concentration, but is used as a constant, makes application of literature values limited and often unrealistic. This is because sorption depends not only of the solute itself (and its concentration), but also on equilibration time, pH, CO_2 pressure, surface area, the type and concentration of other ions in the system, loading capacity of the adsorbing media, temperature and the valence of the ions sensitive to redox changes, as is the case of U (Jenne, 1998).

This explains the variation of K_D values for U sorption for the same soil types across literature, which is summarised in the US EPA report on partitioning coefficients for U (1999). Therefore, derived parameters must be used with caution and use of solid-solution partitioning data is preferred than K_D values. Nevertheless, equilibria studies are relatively rapid and simple methods to provide U sorption parameters over a range

of experimental conditions and will remain popular. The more appropriate approach, is to use the shaken suspension method for preliminary experiments which would be combined with other investigations and pilot studies (Limousin *et al.*, 2007).

1.4.6.3 Measurement of diffusion coefficients

Various methods for measuring diffusion coefficients exist as reviewed by Crank (1975), Shackelford & Daniel (1991) and Shackelford (1990). Half-cell, column and reservoir techniques are popular for radionuclides (Mattigod *et al.*, 2001; García-Gutiérrez *et al.*, 2006; Rakesh *et al.*, 2009; Tokunaga *et al.*, 2004a). In the half-cell method, two half cells are put in contact to allow diffusion of a solute from one cell to another. Such system can be used for the counter-diffusion system if both cells are tagged with the solute, or for salt diffusion if only one half cell is tagged with the tracer. The column method consist of a column containing a fluid with the species of interest; the diffused fraction is measured over time in the effluent in the reservoir and the results are plotted as break-through curves, or as relative concentrations vs time or pore volumes of flow. The reservoir method is similar to column method, however there is no flow-through of the fluid, and single or double reservoirs can be installed (Shackelford, 1990). However, the column method is suitable where convective flow exists (Shackelford, 1991). Shackelford & Daniel (1991) pointed out the discrepancy in definitions of diffusion coefficients across literature, where 50% difference in D -value may exist as a result of different approach (for example, moisture content is or is not included in the equation). Comparison may hence be difficult, and authors should always clearly state the calculation procedure and boundary conditions. Definition of boundary conditions applicable to the aims of the study are important, and so is the selection of appropriate method and mathematical solution (Crank, 1975).

The diffusion coefficient of a solute's diffusion from soil to a sink (e.g. a plant root) can be approximately estimated from self-diffusion experiments. Self-diffusion systems are characterised by no chemical potential gradient in terms of elemental composition but where isotopic (or isotopologue) differences exist. The self-diffusion coefficient provides information on mechanisms of diffusion (Nye, 1966). However, bulk diffusion studies reflect reality better by considering interaction of various ions along the way

towards the root. Nevertheless, the self-diffusion investigations are more popular (Eggenkamp & Coleman, 2009; Laegdsmand *et al.*, 2010; Miyasaka *et al.*, 2014) because they offer a simpler experimental approach (Nye, 1966) and perhaps because the aim of the studies are mostly not specific to root-soil interaction. No specific studies of U diffusion and reactions at a plant root by direct U measurement in intact or re-packed soil were found.

Measurement of time-dependent (transient) diffusion of non-reactive solute is assumed to follow Fick's second law (1-7). The use of non-reactive solutes can help distinguish diffusion from reaction (Laegdsmand *et al.*, 2010). There is a spectrum of (bio)chemical reactions participating in solute diffusion (e.g. dissolution, precipitation, and oxidation-reduction). However, it is only adsorption and radioactive decay that most modelling is concerned about (Shackelford *et al.*, 1991).

Self-diffusion measurement

In self-diffusion, the ion exchanges with its own isotope and the environment is otherwise unchanged. Determination of a self-diffusion coefficient is done by labelling a soil column with the solute of interest and allowing it to diffuse into an identical unlabelled soil column (half-cell method). Another way of conducting self-diffusion measurement is by pulse-labelling the infinitely thin section of a soil column with an (radio)isotope of the solute. Both methods result in concentration-distance profiles following the diffusion down the sink soil column (Nye, 1966).

Soil-labelling was done for many solutes, such as sodium by (e.g. Staunton & Nye, 1983), and various radionuclides (Aldaba *et al.*, 2010b; Aldaba *et al.*, 2010c; García-Gutiérrez *et al.*, 2006), including U (García-Gutiérrez *et al.*, 2006).

Rowell *et al.* (1967) measured the self-diffusion of Cl, Na, Sr and phosphate in a sandy clay loam at various moisture contents using the half-cell method. The study gave strong evidence that diffusion increases with moisture content. Chloride ion was found suitable for measurement of soil impedance factor, which agrees with other studies (Pinner & Nye, 1982; Bagshaw *et al.*, 1972; Staunton & Nye, 1983). The method was successfully used by other authors in measurement of various solutes and radionuclides

with common conclusion that moisture content, impedance factor and adsorption affect diffusion rate (Aldaba *et al.*, 2010a; Aldaba *et al.*, 2010b; Aldaba *et al.*, 2010c; Cole *et al.*, 2000; Laegdsmand *et al.*, 2010; Tokunaga *et al.*, 2017).

Bulk diffusion measurement

To correctly predict diffusion of an ion to a plant root, it is more realistic to consider changes in the flux upon interaction with other ions in the system and those released from the plant root itself (e.g. H^+ or HCO_3^-). This is especially important when the solute of interest is a divalent cation, such as UO_2^{2+} , because of their potentially high mobility (Nye, 1966).

Bagshaw *et al.* (1972) successfully measured phosphate diffusion in soil and compared the calculated diffusion coefficient with phosphate uptake from the soil after 10 days and with desorption experiments. The authors found that the plant-induced changes in soil chemistry (pH) are important in determination of the concentration-distance relationship. Other authors studied bulk diffusion in half-cell system (Rakesh *et al.*, 2009; Vaidyanathan & Nye, 1968). Although studies relevant to U diffusion under nuclear waste disposal conditions are available (Mattigod *et al.*, 2012), no study was found for measurement of U diffusion in rhizosphere relevant conditions by the method.

Kaselowsky *et al.* (1990) studied phosphate bulk diffusion in soil by a half-cell method for a period of 18 days. The authors found it difficult to separate the blocks and decided on the boundary to be where the phosphate concentration was equal on both sides. This shows one of the challenges of the method: the uncertainty for concentrations at the contact boundary which may affect further calculations. The resistance at the boundary would require further mathematical solutions (Crank, 1975). The slope of the curve is sensitive also near the limiting values. However, these values can be considered unimportant as long as they are at about natural background levels. Another half-cell issue is that the method is sensitive to heterogeneities in the moisture content and bulk density (Aldaba *et al.*, 2010a).

The advantage of the method is that it can be used for both constant and concentration-dependent diffusion, and for undisturbed and repacked unsaturated soil (Olesen *et al.*, 2000). The Matano procedure may be applied to deduce concentration-

dependent diffusion coefficients instead of obtaining average diffusion coefficient (Crank, 1975). Moreover, the data from the half-cell method are relatively easy to analyse (Shackelford, 1991).

1.4.7 Modelling of uranium diffusion and reaction in rhizosphere

1.4.7.1 Modelling concepts and purpose

Predictive modelling is an important tool in assessing the potential uptake of a substance (such as radionuclides) by plants. Different models provide different level of complexity but all substantially simplify reality. A good model considers all significant processes but without overcomplicating the problem (Crank *et al.*, 1981).

A common assumption in modelling diffusion in adsorbing medium such as soil is that adsorption and desorption are fast compared with diffusion. This allows sorption to be treated as an instantaneous process and the diffusion deduced accordingly. However, this is erroneous where slow reactions are important in the overall rate of diffusion. Surface diffusion is usually unimportant in soils so this transport mechanism can be ignored in most cases.

Modelling the processes in the rhizosphere is challenging due to an additional array of interactions and dynamic conditions. Luster & Brunner (2006) reviews rhizosphere models, giving pros and cons of each method. Multispecies microscopic models are probably the best suited for rhizosphere conditions. They consider the bulk diffusion interactions of co-diffusing ions. However, they often neglect important factors such as changing pH and release of organic acids. Radial and longitudinal root geometry should be accounted for in the models as the root creates different chemical changes along its axis (Luster & Brunner, 2006).

1.4.7.2 Review of existing models

Empirical models

Empirical models are based on empirical observations and subsequent modelling of sorption of the solute or transfer factors from soil-to-plant (discussed earlier). The

sorption process at constant temperature is generally described by a curve (hence the name isotherm).

The simplest form of the expression of solute mobility is the distribution coefficient, K_D . The K_D is the ratio between the substances contained in the solid phase via adsorption and that in solution under the experimental conditions at the adsorption equilibrium:

$$K_D = \frac{C_S}{C_L} \quad (1-15)$$

The K_D expression of sorption characteristics has many limitations (section 1.4.6). Modelling should use sorption parameters expression as solid-solution partitioning over the relevant range of concentrations, not just single K_D values.

Uranium sorption is typically nonlinear with concentration (Missana *et al.*, 2004). Commonly, Freundlich (Dong *et al.*, 2006; Hull *et al.*, 2002) and Langmuir isotherms (Rout *et al.*, 2014; Solgy *et al.*, 2015) are fitted either in their linearised or non-linear form (Chen, 2015). The Freundlich isotherm describes adsorption as a two parameter exponential function. The Langmuir isotherm assumes that the solid has limited adsorption capacity, and that each free site can react with the solute and form a surface complex (Limousin *et al.*, 2007). Other studies work with composite isotherms (i.e. the adsorption curve is broken into two or more isotherms) (Braithwaite *et al.*, 1997; Ping *et al.*, 2014) or are based on surface complexation modelling (Bachmaf & Merkel, 2011; Cheng *et al.*, 2006; Fox *et al.*, 2006; Rihs *et al.*, 2014). All these approaches assume U interchange equilibrium, which is not likely in natural soil systems. Review of different empirical models is beyond the scope of this thesis is provided by other authors (Limousin *et al.*, 2007; Sparks & Suarez, 1991).

However, it is desorption, not only adsorption, that indicates potential for solute uptake by plants. The rate and extent of desorption from the soil solid controls the solute concentration in solution available for root uptake. Molina Millán *et al.* (2006) compared methods for measuring metal (nickel) desorption from soils for parametrising rhizosphere models. The authors concluded that the repeated extraction from shaken suspension at constant soil-solution ratios is too tedious, and varying the soil-solution

ratios is preferred. They also warn that in methods using a sink (in a form of a resin added in the solution) the assumed equilibrium might be altered by the resin presence compared to real soil conditions.

Molina Millán *et al.* (2008) also pointed out that desorption is sensitive to factor such as the type and strength of the background electrolyte and presence of organic agents produced by a root and microbes. Therefore measurements must be done under conditions representing the system to be modelled. The desorption is modelled by the same isotherms as adsorption.

Mechanistic models

Mechanistic models of transport and speciation in the rhizosphere exists but none has become widely accepted for strongly sorbing solutes such as many radionuclides. For example, the RhizoMat model (Szegedi *et al.*, 2008) includes speciation in the soil solution and considers both planar and radial geometry of the root and many parameters can be manually modified. The model performance was found satisfactory when compared to other codes and experimental data. However, the authors of the model recognised its various limitations and the need for further development. It has never been tested for uranium.

The model of Jacques *et al.* (2008) is specific to U and considers many important processes. However, it is limited to acidic conditions and assumes fixed low CO₂ pressure. In addition, the model is not intended for rhizosphere studies. In contrast, Pérez-Sánchez & Thorne (2014a) offer a model which is intended for U behaviour in soils and uptake by plants. However, the model is not intended for rhizosphere, allows mainly for convection and uses K_D values, and is intended for long-term predictions.

Kirk (2002) provides a model of root-induced solubilisation of nutrients, which has been tested for phosphorus (P) with good results. Kirk with his collaborators provides further models of solute solubilisation and uptake by plants (e.g. Kirk, 1999; Kirk & Solivas, 1997; Zygalkakis *et al.*, 2011). The collection of his work provides good direction for model development for U. Relevant information and models which would be useful in U model development are available (e.g. Leitner *et al.*, 2010; Tinker &

Nye, 2000). The series of papers 'Measurement and mechanisms of ion diffusion in soil' by P. H. Nye and his colleagues is very useful to understand the important processes.

The literature review revealed no existing model ready to be applied for U transport and uptake by plants. As part of the Lo-Rise programme, Boghi *et al.* (2018) developed a mechanistic model intended specifically for uranium and rhizosphere; however the model has been yet lacking testing against experimental data.

Boghi *et al.* (2018) developed a mathematical model of U uptake by plants which allows for root-induced changes in soil chemistry. The model uses equations for transport and reaction of U. The model works with acids and basis around the root, U speciation with hydroxyl, carbonate and organic ligands, and sorption kinetics. Root-induced changes in soil pH and CO₂ pressure and two-dimensional root geometry are also included. The sensitivity analysis of the model showed that all the above parameters must be included in U uptake models. The effect of soil moisture content, pH and CO₂ pressure, and slow reactions suggested were especially important. The model appears promising and applicable to other radionuclides.

1.4.7.3 Assessment of uranium transport models

Modelling provides a great shortcut in the assessment of contaminant mobility and uptake by plants. More importantly, mechanistic modelling aids testing of the understanding of the dynamics of a given system. Once the system is well understood, practical simplified models can be developed. However, the models must be rigorously tested and applied only to validated conditions and contaminants. Most recent studies combine shaken suspension experiments and equilibria modelling but this approach is not satisfactory. Empirical models offer a poor approach often neglecting reaction kinetics and other important factors. The modelling outcomes could mislead decision-makers to address U contamination. The frequent use of distribution coefficient (K_D) is especially inadequate for rhizosphere complexity (although K_D might be a useful indicator for other purposes).

Mechanistic models are preferred but they need to consider all important processes including system composition and conditions, U speciation, simultaneous transport of several ions and their interactions, and reaction kinetics. Microscopic rhizosphere

models based on pioneering work of Nye and his colleagues offer the best approach to date. The models of solute transport and availability for uptake by plants have to be tested against experimental data which would describe simultaneously transport-controlled and chemical kinetics phenomena (Sparks, 1999), not against empirical data. The model of Boghi *et al.* (2018) appears to be one of the best models available, and is especially tailored for U. Therefore, it merits experimental validation.

1.4.8 Chapter conclusions

There is an extensive literature available on U transport and reactions (mostly in separation) in soils and models are available for assessment of U mobility. But key gaps and limitations remain. Particularly:

- The majority of U sorption studies are limited to single mineral surfaces, not a heterogeneous soil media, and are often intended for the subsurface environment, such as nuclear waste repositories.
- Uranium transport measurements in soils (and sediments) mostly ignore the plants ability to change soil chemistry causing U solubilisation, and hence enhanced transport and phytoavailability. Alternatively, they study only plant effects in isolation.
- Most studies use simple empirical models which only describe the assumed final state of the system, ignoring important reaction rates and U transport limitations.
- More advanced models (which consider soil properties, soil solution composition, reactions and their rates involved) are generally not transferable to other systems and radionuclides, especially to the rhizosphere.
- No studies were found which would combine comparison of the most commonly used empirical models, realistic diffusion measurements, and application of more sophisticated mechanistic models.
- The mathematical model of Boghi *et al.* (2018) offers a novel and robust approach to predict U transport and uptake by plants. Testing of the model against data from measurements of realistic U diffusion with reaction is desirable.

This doctoral thesis addresses all the issues above.

CHAPTER TWO

Comparison of methods for measuring solute diffusion coefficients in soil

Summary

Two methods for measuring solute diffusion in soil are compared: (a) a pulse-addition method in which a column of soil is pulsed with a trace addition of a non-adsorbing solute is made to one end and concentration-distance profiles measured after a suitable interval; and (b) a half-cell method in which two soil columns are put together (one containing known amount of non-adsorbing solute and the other is free of the solute) and diffusion allowed after which concentration-distance profiles are plotted. The pulse addition method allows analysis with a simple solution of the diffusion equation to obtain the soil diffusion coefficient for the solute, so is preferred. The non-adsorbed solute, bromide, was used to simplify analysis of the results. The results confirmed that the pulse-addition is simple and reliable and more robust than the half-cell method. The concentration-distance profiles measured with the half-cell method were well-predicted using the diffusion coefficient determined by the pulse method, but not vice-versa. However, the half-cell method is suitable where solute sorption is time- or concentration-dependent.

2.1 Introduction

Conventional models of solute diffusion in soil are based on Fick's first law of diffusion which relates the flux, F , of a solute through unit cross-section of soil to the concentration gradient, $\partial C / \partial x$, across the cross-section: $F = -D \partial C / \partial x$ where D is the solute diffusion coefficient in the soil, which is averaged over microscale variations (Nye, 1979). Various methods exist for measuring solute diffusion coefficients so defined, and the factors that contribute to differences in values between solutes and soils (Moldrup *et al.*, 2001; Staunton, 2008; Albada *et al.*, 2010a).

The simplest approach is to measure the fraction of diffusant that moves from a source to a sink in a given time, and to analyse the results with the appropriate solution of the diffusion equation. This has the attraction of simplicity. But it will give misleading information if the diffusion coefficient is concentration- or time-dependent, for example due to non-instantaneous reactions or slow access to sorption sites. Further, it will not detect errors due to non-homogeneities in the soil, or poor source-soil contact which may cause a barrier to diffusion.

A more reliable though laborious approach is to measure concentration-distance profiles of the diffusant through the soil, and to fit the solution of the diffusion equation to the measured profiles, subject to the appropriate boundary conditions. Non-homogeneities and poor source-sink contact are therefore more easily detected, and the diffusion coefficient is derived from many concentration measurements, not just a single measurement of the source, so it is more reliable. Further, in principle, concentration- and time-dependencies can be assessed, although in practice that generally requires numerical solution of the diffusion equation.

In this paper we compare alternative approaches for determining diffusion coefficients based on measurements of concentration-distance profiles. We compare the 'pulse-addition' method, in which a trace amount of solute is placed on one end of a soil column and the resulting concentration-distance profile through the soil is determined; with the 'half-cell' method, in which two columns of soil containing different

concentrations of the solute are placed in contact and the resulting concentration-distance profiles in each cell is determined.

The pulse-addition method has the advantage that if the diffusion coefficient is constant, the solution of the diffusion equation has a simple form with which the diffusion coefficient can be determined very accurately (Pinner & Nye, 1982). The half-cell method is more cumbersome but has the advantage that concentration-dependent diffusion can be studied, including the effects of solute desorption in the source cell versus adsorption in the receiving cell (Olesen *et al.*, 2001). We compare these two methods by studying the diffusion of a non-adsorbed solute, for which, in principle, the diffusion coefficient should be constant. We aim to draw conclusions about the suitability and accuracy of each methods for different applications.

Theory

Transient-state diffusion in one dimension is described by:

$$\frac{\partial C}{\partial t} = \frac{\partial}{\partial x} \left(D \frac{\partial C}{\partial x} \right) \quad (2-1)$$

where C is the solute concentration in the whole soil and D is the diffusion coefficient. If diffusion along the soil solid is unimportant, as in general it will be (Chapter 1), then

$$D = D_L \theta f_L \frac{dC_L}{dC} \quad (2-2)$$

where D_L is the solute diffusion coefficient in free solution, θ is the volumetric soil moisture content, f is an impedance factor and C_L is the solute concentration in the soil solution. A constant diffusion coefficient requires that dC_L/dC is constant over the relevant concentration range. For a non-adsorbed solute, $C = \theta C_L$ and hence in Equation (2-2) $\theta dC_L/dC = 1$ and $D = D_L f$.

Pulse-addition method

A trace amount of the solute is deposited instantaneously on the planar surface of a semi-infinite soil column. The boundary conditions are

$$\begin{aligned} C &= C_1 & x &= 0 & t &= 0 \\ C &= C_0 & x &> 0 & t &= 0 \\ C &= C_0 & x &= \infty & t &\geq 0 \end{aligned} \quad (2-3)$$

where $x = 0$ is the source boundary and $x = \infty$ is the semi-infinite far-field boundary and C_0 is the initial concentration in the sink cell. If D is constant, the solution of Equation (2-1) subject to these conditions is (after Crank, 1975, Equation 2.7)

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

where C is the concentration at distance x from the surface at time t . Thus a graph of $\ln(C - C_0)$ against $x^2/4t$ should have slope $-1/D$ and intercept $\ln(C_1 - C_0)$. If the applied solute is a trace amount of an isotopologue of the solute, then D is the solute's self-diffusion coefficient in the soil. For a non-adsorbed solute, such as Br^- , $D = D_L f$ and therefore $f = D/D_L$. D_L for $\text{Br}^- = 2.08 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ (Lide *et al.*, 2009). This is the method of Pinner & Nye (1982).

Half-cell method

Two half-cells containing different concentrations of the solute are placed in contact. The boundary conditions are

$$\begin{aligned} C &= C_1 & x &< 0 & t &= 0 \\ C &= C_0 & x &> 0 & t &= 0 \\ C &= C_1 & x &= -\infty & t &\geq 0 \\ C &= C_0 & x &= \infty & t &\geq 0 \end{aligned} \quad (2-5)$$

and the solution of the diffusion equation for constant D is (after Crank, 1975, Equation 2.14)

$$\frac{C - C_0}{C_1 - C_0} = \frac{1}{2} \operatorname{erfc} \left(-\frac{x}{2\sqrt{Dt}} \right) \quad (2-6)$$

For a sorbed solute, if $C_1 > C_0$, in the region $x < 0$ diffusion is accompanied by desorption from the soil solid, whereas in the region $x > 0$ it is accompanied by adsorption. Any real or apparent hysteresis in sorption will be revealed. However, for non-sorbed solutes, or sorbed solutes for which sorption is independent of concentration and time (i.e. D is constant), concentration-distance profiles should obey Equation (2-6) and hence fits of Equation (2-6) can be used to obtain the value of D . If D is concentration-dependent, concentration-distance profiles must generally be analysed by cumbersome numerical solutions of the diffusion equation.

In the rest of the chapter, the pulse-addition and half-cell methods are compared. The methods are analysed using the corresponding equations above, as applied to the simple case of the counter-diffusing of two non-adsorbed solutes against each other. These methods and analyses will also apply to the self-diffusion of isotopes of a sorbed solute as long as the isotopic exchange is instantaneous, and the counter-diffusion of different sorbed solutes as long as their exchange is not concentration- or time-dependent.

2.2 Materials and methods

2.2.1 Preparation of diffusion cells

Samples of topsoil (0–20 cm depth) of a typical brown earth (Wick series from Henfaes Research Centre, Bangor University, Abergwyngregyn, Gwynedd) were 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, cation exchange capacity = 10.2 $\text{cmol}_c \text{ kg}^{-1}$, organic C content = 30.2 g kg^{-1} , clay content = 145 g kg^{-1} , silt content = 328 g kg^{-1} and sand content = 527 g kg^{-1} . The soil was washed three times with 10 mM CaCl_2 at a solution to soil ratio of 5:1, discarding the supernatant after each washing and finally air

drying and re-sieving to < 0.5 mm. The soil was identified as suitable for the experimental work due to its low U and clay content and no P fertilisation history. Therefore complicating reactions were not expected.

Pre-weighed amounts of the air-dry soil were packed into 2.9-cm internal diameter, 3-cm long Perspex cylinders to a pre-set bulk density ($\approx 1.42 \text{ g cm}^{-3}$). To achieve uniform packing, the soil was poured in small amounts into the cylinder and, after addition of each layer, evenly distributed with a brush and pressed down with a plunger while rotating the cylinder. To prevent formation of layering, the surface of the pressed layer was disturbed with a brush to mix well with the following layer. The soil was then gradually saturated from the lower end with 10 mM CaCl_2 so that as far as possible entrapped air was displaced. This was achieved by placing the cell packed with soil in a Petri dish containing the solution so that the solution level and the cell height were nearly identical in order to prevent hydraulic issues. Saturation time was initially determined by monitoring mass changes until no further change was observed. The cylinders were then brought to the desired water content on a pressure plate for 10 days. They were then incubated in a water-saturated atmosphere for 4 hours and then diffusion coefficients measured as below. Preliminary tests to confirm homogenous soil packing and moisture content were done by sectioning randomly selected soil columns (Appendix A-1). The slices were oven dried (for 24 h at 105°C) and moisture-distance profiles were plotted based on the wet and dry weight difference and calculated ρ .

2.2.2 Pulse-addition method

Cells of soil so prepared were pulse-labelled with a trace amount of Br^- and the resulting profiles of Br^- concentration through the soil determined. Pulse-labelling was achieved by moistening a piece of cellulose acetate membrane of the same diameter as the cell with 10 mM CaCl_2 containing 4.7×10^{-6} mol of CaBr_2 , and placing it against one end of the cell. It was then held in place with tweezers. After 5 minutes, the membrane was removed, and the cylinder was incubated at 20°C for 2 hours wrapped in Parafilm to prevent drying out and allowed the Br^- pulse to diffuse into the soil. The soil was then sectioned at approx. 0.5 mm intervals parallel to the labelled surface using a microtome (Griffin and George DIEH 600-B) and a stainless steel blade. A total of approx. 2 cm of

the soil column was sectioned. The moisture content of the remaining soil was pre-determined at the end of moisture equilibration in pressure cells.

The soil sections (approximately 1.0 g moist weight) were transferred quantitatively to 15 cm³ plastic centrifuge tubes, weighed, and shaken end-over-end for 30 min with 0.01 M CaCl₂ at 1:10 soil solution ratio. The suspensions were centrifuged at 3,500 *g*, filtered through 0.45 µm filter paper, and Br⁻ in the filtrates measured by ICP-MS (PerkinElmer NexION 350, Boston, MA, USA). The thicknesses of the sections were calculated from their weights and the mean bulk density of the soil in the cylinder. Four replicate runs were made per each repeat run. Runs were made at a range of moisture contents near field capacity and bulk densities in the range 1.3–1.5 g cm⁻³.

The measured concentration-distance profiles were analysed by regressing $\ln C$ against $x^2/4t$ and obtaining $-1/D$ from the slope of Equation (2-4), and hence f from $f = D/D_L$. The background Br concentrations were determined by iteratively fitting Equation (2-4) to the data, rejecting data far from $x = 0$ with each iteration until all the remaining data were within two standard deviations of the predicted values (Matsullat *et al.*, 2000). The fits were made using the linear regression routines in SigmaPlot 11.0 (Systat Software Inc, Chicago, IL, USA).

2.2.3 Half-cell method

For each run, two half-cells of soil were prepared, one with 0 mM CaBr₂ in 10 mM CaCl₂ in the soil solution and the other with 0.15 mM CaBr₂ in 10 mM CaCl₂. The CaBr₂ addition was made when initially wetting-up the soil before bringing it to the target water content on a pressure plate. The half-cell unit was then fixed in place with electric tape to ensure good contact between the cells and wrapped in Parafilm to prevent drying out. The combined unit was incubated at 20 °C for 4 hours. The cells were then separated, the cores frozen in liquid nitrogen and sectioned 1 h later using the same procedures as for the pulse-source method. The sections were oven dried at 105 °C for 24 h and later analysed for Br content as in pulse-addition method. Three replicate runs were made.

The measured concentration-distance profiles were analysed by fitting Equation (2-6) to the data to obtain C_1 , C_0 and D , and hence f from $f = D/D_L$. The fits were made using the MS Excel Solver program (Microsoft Corp, Redmond, WA, USA), minimizing the sum of squared deviations (SSD) between the measured data and fits to the equation using the GRG Nonlinear method. Outliers were eliminated based on standardized residuals > 2 of the initial Solver fit to the entire dataset. Standardised residuals are residuals divided by the standard deviation of the entire residual population. Any value outside a certain range, usually above +2 or below -2, can be used to indicate an outlier.

2.3 Results

2.3.1 Pulse-addition method

Figure 2-1 shows measured concentration-distance profiles of Br^- through the soil for two replicate runs and Figure 2-2 shows the data plotted according to Equation (2-4). Further replicates were prepared but rejected either due to insufficient number of data points left after background data removal or poor linearity of the fit (Appendix A-2). The agreement with Equation (2-4) was excellent. The fits were made after elimination of background data and outliers. Figure 2-3 shows potential error in f due to incorrect specification of background values and outliers.

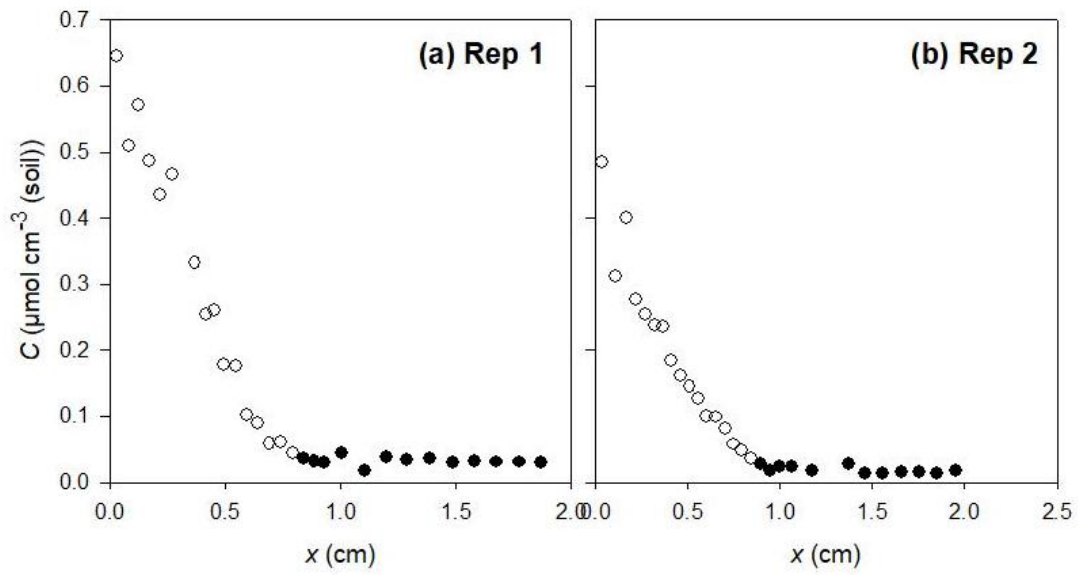


Figure 2-1 Concentration-distance profiles of Br^- (C) following a pulse addition of Br^- to one end of a moist soil column. The background C values (filled circles) were determined by iteratively fitting Equation (2-4) to the data until all non-background data agreed with the fits to within two standard deviations (Methods).

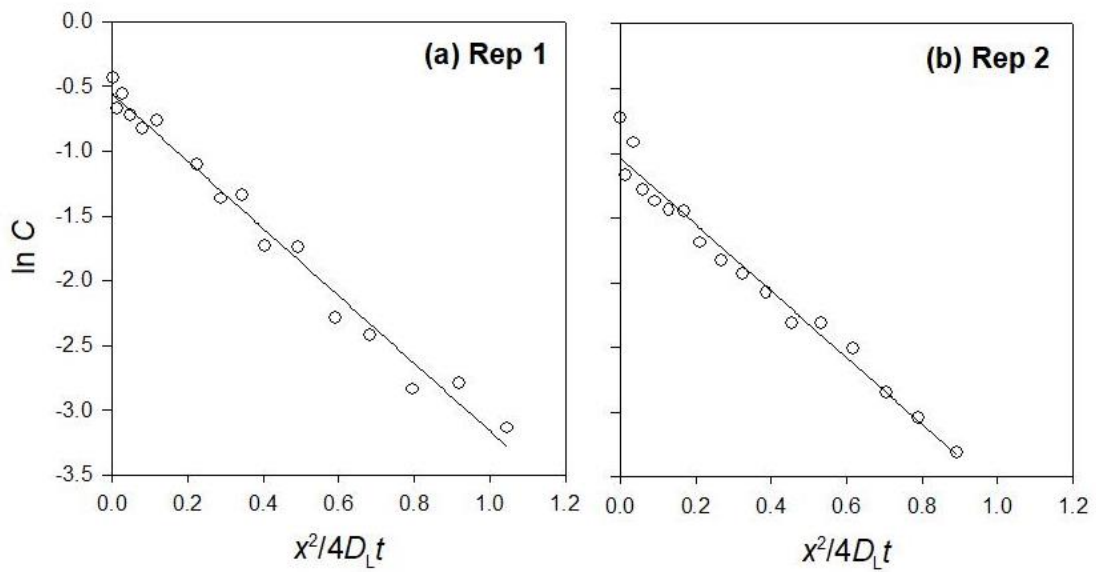


Figure 2-2 Concentration-distance profiles of Br^- from Figure 2-1 plotted according to Equation (2-4). Data are measured concentrations; lines are fits to Equation (2-4). **(a)** Rep 1 was packed to $\rho = 1.45 \text{ g cm}^{-3}$, $\theta = 0.44 \text{ cm}^3 \text{ cm}^{-3}$, and **(b)** Rep 2 to $\rho = 1.46 \text{ g cm}^{-3}$, $\theta = 0.38 \text{ cm}^3 \text{ cm}^{-3}$, and the corresponding fitted value of f were 0.38 ($r^2 = 0.98$) and 0.39 ($r^2 = 0.97$).

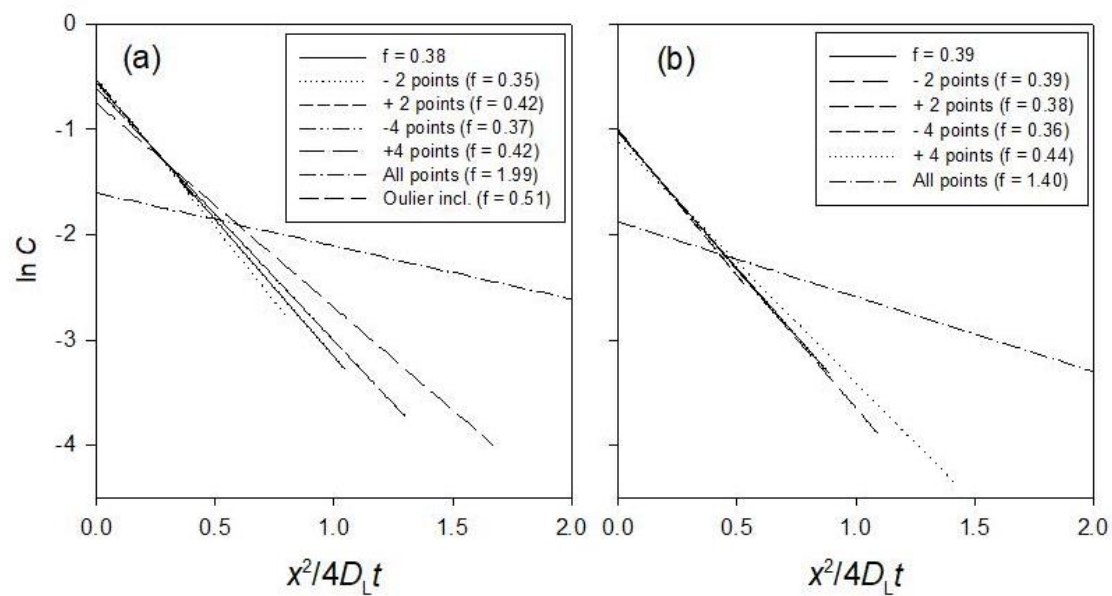


Figure 2-3 Sensitivity of fitted f -values to the assessment of background concentration values and outliers for **(a)** Rep 1 and **(b)** Rep 2. Solid lines are the fits in Figure 2-2; broken lines are the fits with the indicated assessment method.

2.3.2 Half-cell method

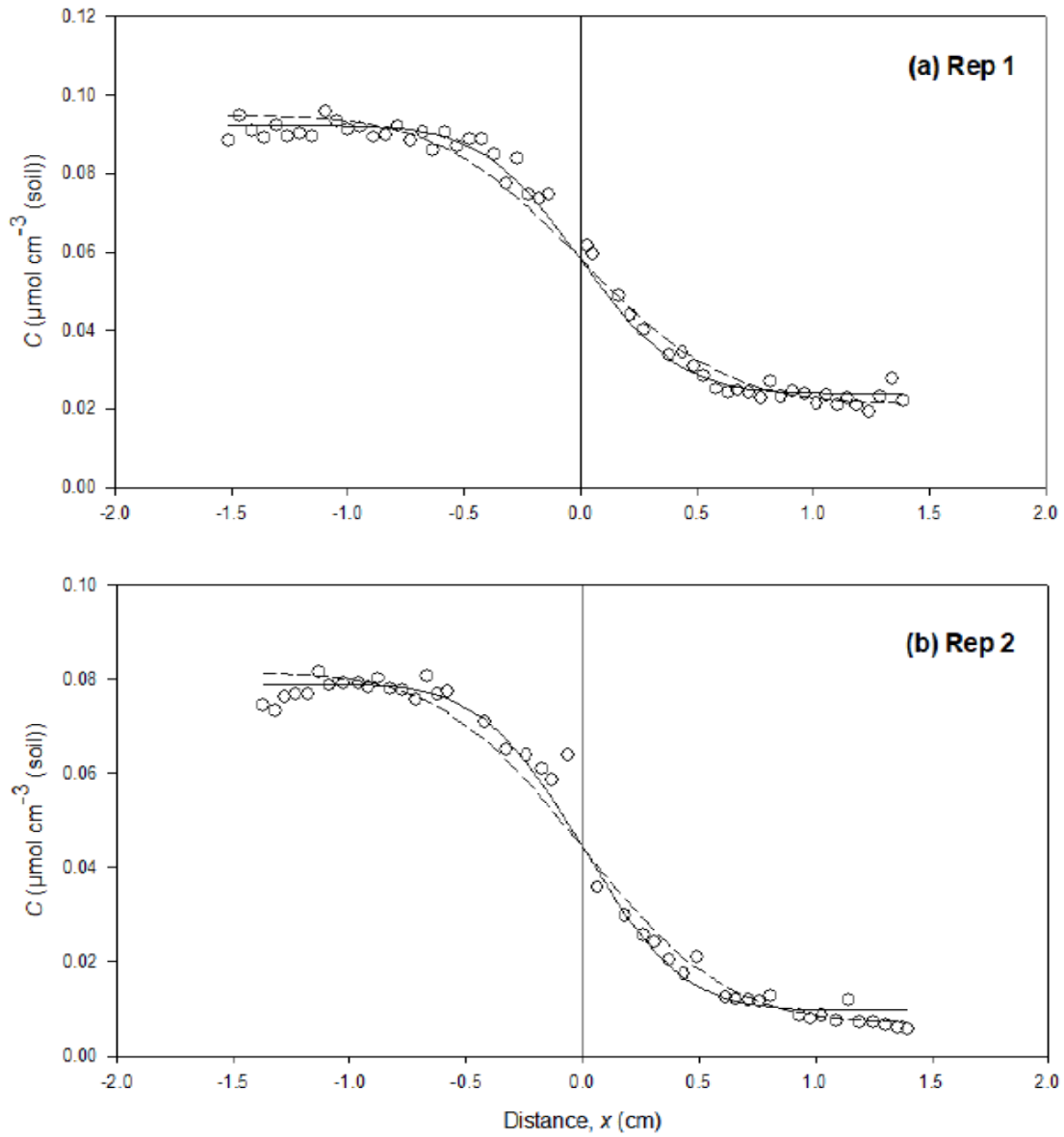


Figure 2-4 Concentration-distance profiles of Br^- through soil measured by the half-cell method. Data are measured concentrations; lines are fits to Equation (2-6) with either no constraints (solid lines) or with f set at the value obtained by the pulse-addition method ($f = 0.39$; dotted lines). The fitted f without constraints was 0.19 for both replicates. Soil bulk density, $\rho = 1.42 \text{ g cm}^{-3}$; moisture content, $\theta = 0.36 \text{ cm}^3 \text{ cm}^{-3}$ for both replicates.

Figure 2-4 shows concentration-distance profiles measured using the half-cell method with fits of Equation (2-6) to the measured data. There were only minor differences in ρ

and θ within and between the replicate half-cells ($sd \leq 0.01$). The two lines in Figure 2-4 are (a) with Equation (2-6) fitted to the data (excluding outliers) without constraints, giving $f = 0.19$; and (b) with Equation (2-6) fitted to the data (excluding outliers) with f set at the value obtained with the pulse-addition method ($f = 0.39$). Figure 2-4 compares the goodness of fit of Equation (2-6) to the data in this way.

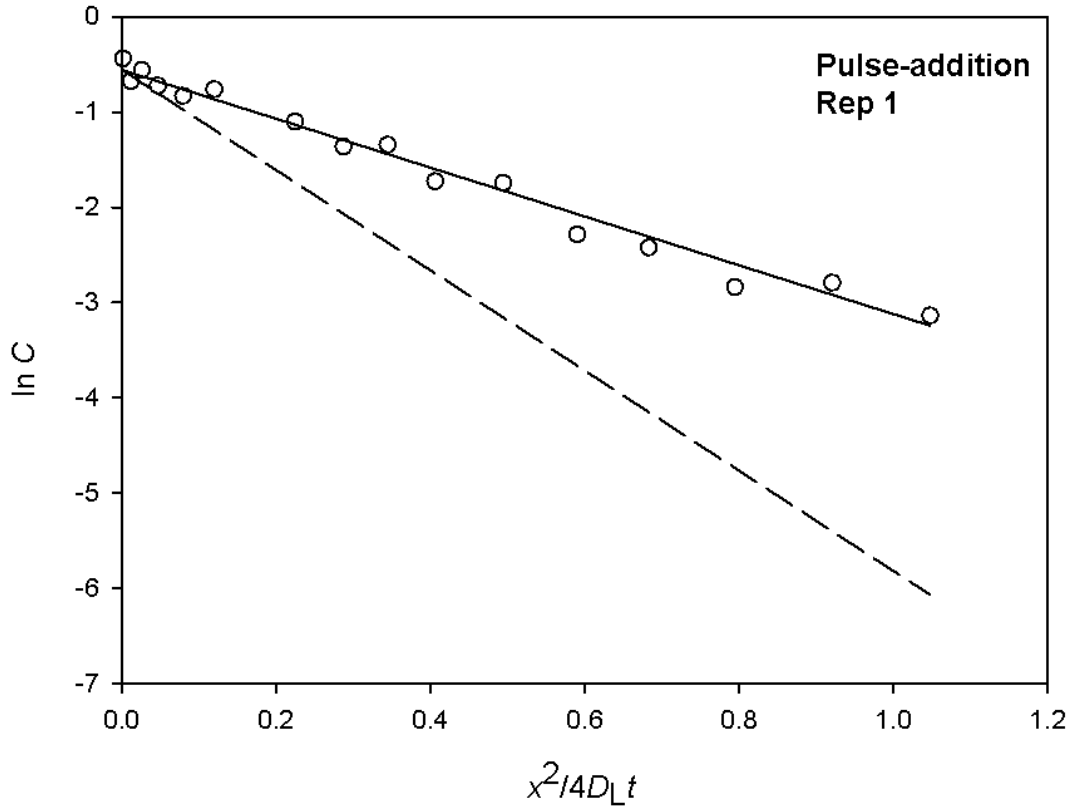


Figure 2-5 The $f = 0.19$ from half-cell fitted to Equation (2-4). Circles are observed values for pulse-addition Rep 1. The solid line is a fit of pulse-addition f -value ($f = 0.19$); the broken line is a fit of half-cell f -value ($f = 0.39$).

2.4 Discussion

2.4.1 Methods comparison

The pulse-addition is a simple method of measurement of diffusion coefficient and it is highly reliable when D is constant (i.e. it is not changing with concentration). The good fits and high reproducibility of the results to Equation (2-4) (and the agreement between

the f values obtained in replicate runs indicate the experimental methods were sound and the theory correct.

The obtained $f = 0.39$ value is within the ranges reported by others for sandy to loamy soils at similar bulk densities and moisture contents (Rowell *et al.*, 1967; Moldrup *et al.*, 2001). The approach of counter-diffusing Br^- against Cl^- has additional advantage of elimination of (radio)isotopes hence simplifying the analytical procedure and reducing costs.

The impedance factor from the pulse-addition method was used to evaluate the half-cell method. To do so, the results were fitted from the half-cell method with the f obtained from pulse-addition by constraining Solver to $f = 0.39$ (Figure 2-4). The fits were in good agreement with the observed data with relatively small SSD similar to the unconstrained fits. When applied vice-versa (i.e. fitting the unconstrained f -value from half-cell to Equation (2-4), the disagreement of the half-cell value became apparent as shown in Figure 2-5. The soils in the two methods differed only slightly in ρ and θ . It is unlikely the variation could lead to such a difference in f . In addition, the half-cell f -value is unrealistic when compared to literature. The $f \approx 0.20$ is representative of rather clay dominated soils of similar moisture content (Pinner & Nye, 1982; Staunton & Nye, 1983). Therefore, we rejected the half-cell f -value for modelling purposes.

Differences in measured D , (which is a function of f), of such magnitude (and higher) between half-cell and pulse-addition methods were reported elsewhere (Aldaba *et al.*, 2010b) although with opposite trend. The authors concluded better transfer between the half-cells than from the filter paper source. It was also noted that excess amount of Br^- was needed to observe good diffusion profiles in pulse-addition. In contrast, in half-cell method, the Br^- addition resulted in $< 1\%$ of the added Cl^- in the soil. In both methods, the naturally occurring Cl^- (reported 2.2 Meq L^{-1} for sandy loam soils (Tinker & Nye, 2000)) and that introduced from soil washing was high enough to prevent salt diffusion and to comply with self-diffusion principles.

However, the very low Br^- concentration in half-cell method is the likely reason for such a low f . From theory, the non-reactive solute diffusion is concentration

independent. In practice, it is not easy to reliably apply the half-cell method at Br concentrations near background where correct estimation of C_0 becomes difficult and may alter the results (Crank, 1975). The problem of low concentration becomes irrelevant where background solute concentration is negligible compared to solute addition, or where two isotopes diffuse against each other.

Nevertheless, the unconstrained fits of the diffusion profiles to Equation (2-6) were in perfect agreement in f (Figure 2-4). The smoothness of the fitted curves confirms good packing technique giving uniform θ and ρ , homogeneous Br distribution in source cell and good contact between the source and sink cells which is a common challenge (Aldaba *et al.*, 2010b; Shackelford, 1990; Tokunaga *et al.*, 2017).

Therefore, the half-cell method has a potential for application where diffusion is not linear, which is a common case of contaminants due to multiple-species diffusion (i.e. bulk diffusion) and their concentration- and time-dependent reactions and sorption processes. Therefore the half-cell method is useful to test predictive models of non-linear diffusion scenarios with model parameters determined independently.

2.4.2 Methodological considerations

The effect of inadequate treatment of background and outliers and poor slicing technique could significantly alter the results (Zhang, 2010) as demonstrated in Figure 2-1 and Figure 2-3.

Soil sectioning is more precise if quick freezing is applied and was recommended elsewhere (Barraclough & Nye, 1979). The application of soil freezing ensures (a) solute immobilisation and hence no further diffusion during slicing, (b) the soil losses and disturbance to the surface reduced to minimum, and (c) elimination of an error introduced from calculation of distance and concentration based on wet weight of each slice. The solute immobilization can be important where short diffusion time is applied and/or where diffusion is fast, as may be the case for non-reactive solutes.

The quantification of the natural background requires an appropriate statistical approximation with a method robust enough to distinguish the background from a small

concentration gradient. The iterative 2σ -technique was selected for its simplicity and validation by other authors (Matsullat *et al.*, 2000). The background corresponded the breaking point in linearity of the $\ln C$ against $x^2/4D_Lt$ at approx. 0.8 cm distance from the source for both replicates but with 25 % difference in concentrations. This is significant at low solute concentration and average values from blank samples should be avoided.

The slope of the linear plots in pulse-addition is sensitive to outliers, as shown in plot (a) in Figure 2-3 showing the effect of a single outlier with f increasing from 0.39 to 0.51. However, the diffusion profiles presented had good linearity and little scatter and hence the method remained robust with f deviating by no more than ± 0.05 when up to four points were added or removed from calculated threshold. Therefore, the method withstands slightly incorrectly determined background as long as the dataset has overall smooth trend and is large enough.

2.5 Conclusions

We compared two methods for measuring of diffusion coefficients in soil to evaluate their suitability for different applications. We found that:

- The simplicity and reliability of the pulse-addition method makes it preferable for measurement of diffusion coefficients of nonreactive and non-sorbing solutes, i.e. where D is constant.
- The half-cell method is suitable where D is concentration- or time-dependent due to time- or concentration-dependent sorption processes.
- Both methods are sensitive to non-homogeneities in the soil bulk density or moisture content and require careful soil preparation and sectioning, and background and outlier identification.

CHAPTER THREE

Measurement of uranium sorption in shaken suspensions

Summary

The solid-solution partitioning of U was measured in shaken suspensions of the experimental soil at different pHs and CO₂ pressures. The results agreed with the generally-observed strong dependence of U sorption on pH and CO₂ pressure, with a bell-shaped relation between sorption and pH linked to differences in U speciation. The relation between U sorbed and U in solution at each pH and CO₂ pressure was satisfactorily described with a Freundlich-type equation. The sorption parameters so determined were used to calculate concentration-distance profiles of U through the soil in the half-cell U diffusion experiments presented in Chapter 4, assuming a constant U diffusion coefficient for each soil pH and CO₂ pressure as indicated by the U buffer power from the sorption parameters at the initial soil U concentration. These were compared with the predictions of a more-exact model allowing for both the concentration- and time-dependence of adsorption and desorption, which is presented in Chapter 4. The results showed diffusion was not very sensitive to differences in the buffer power over the relevant U concentration range, but was very sensitive to differences with pH and CO₂ pressure. Diffusion was also sensitive to the time-dependence of adsorption and desorption allowed for in the more-exact model. Shaken suspension measurements will not reliably capture such time-dependency because sorption is artificially accelerated by disaggregation and convection.

3.1 Introduction

3.1.1 Background

Uranium transport in soil toward a plant root occurs mainly by diffusion because dissolved U concentrations are typically too small for significant mass flow at typical water flows into roots. Mechanistic models of U uptake by roots therefore need to be based on diffusive movement and this requires quantification of soil diffusion coefficients. The components of the soil diffusion coefficient, D , of a particular solute are indicated by the relation (Tinker & Nye, 2000)

$$D = D_L \theta f dC_L/dC \quad (3-1)$$

where D_L = the diffusion coefficient of solute in free solution, θ = soil volumetric water content, f = diffusion impedance factor, C = whole soil concentration of solute and C_L = concentration in solution (Chapter 1). The derivative dC_L/dC is the inverse of the ‘buffer power’ for the solute, and depends on sorption processes controlling its solid-solution interchange.

Generally, sorption is a reversible process, but the rates of adsorption and desorption are not necessarily the same. Hence there is often apparent hysteresis in adsorption-desorption isotherms (Tinker & Nye, 2000). Typically, the initial rapid adsorption or desorption of U is followed by a continuing slow adsorption or desorption (Braithwaite *et al.*, 1997; Ball, 2009; Qafoku *et al.*, 2005).

In addition, both U adsorption and desorption are functions of U concentration as well as pH and CO₂ pressure as they influence U speciation changes due to complexation with organic and inorganic ligands (Mitchell *et al.*, 2013; Pérez-Sánchez & Thorne, 2014a). Therefore, application of empirical equilibrium models with constant distribution coefficient constants, K_D , is likely to be inadequate in models of U diffusion. Shaking the soil in a set volume of electrolyte solution containing a known amount of U until sorption equilibrium is assumed might disguise and alter sorption kinetics and hence reversibility. Empirical models based on such approaches will be unreliable where sorption kinetics are important.

Most measurements of U solid-solution interchange are done for adsorption in shaken soil suspensions because this is easier. However models of diffusion to roots require information on desorption rather than adsorption. It is difficult to measure U desorption reliably because it is sensitive to measurement conditions, particularly the solid-solution ratio used (Ping *et al.*, 2014) and the nature of any sink added to remove desorbed U, such as an exchange resin (Molina Millán *et al.*, 2006). Further, in shaken suspensions sorption is artificially accelerated by dispersal of the soil and convection (Sparks, 1999).

In the work described in this chapter it was sought to test the null hypothesis that U diffusion in soil at a given pH and CO₂ pressure can be reliably predicted with a constant U diffusion coefficient, without allowing for its concentration- and time-dependence. I had the following specific objectives toward testing the null hypothesis.

- To measure the soil solid-solution partitioning of U in shaken soil suspensions at the range of U concentrations relevant to the experiments in Chapter 4, in which concentration-distance profiles of U diffusing through soil are measured.
- To measure the above under the range of pH and CO₂ partial pressures in the experiments in Chapter 4.
- To measure sorption kinetics in shaken soil suspensions.
- To fit the results of the above measurements to suitable sorption equations, with which to calculate soil U buffer powers and hence diffusion coefficients under the conditions of the experiments in Chapter 4.
- To formulate a model with which to predict U concentration-distance profiles in soil assuming a constant diffusion coefficient, and to compare it with the more-exact model presented in Chapter 4, which allows for concentration- and time-dependence of adsorption and desorption.

3.2 Materials and methods

3.2.1 Speciation modelling

Uranium speciation in solution was calculated using Visual MINTEQ 3.1 (Gustafsson, 2012) to determine the most important species under ambient and elevated (5 kPa) CO₂

pressures. The input species were Ca^{2+} , UO_2^{2+} , Cl^- , NO_3^- and CO_2 at concentrations representing conditions in the sorption experiments. Carbonate ligands (H_2CO_3 , HCO_3^- , CO_3^{2-}) were calculated from the CO_2 pressure in MINTEQA2 3.1 (Gustafsson, 2012).

3.2.2 Shaken suspension experiments

The experimental soil was the same soil as in Chapter 2 and prepared in the same way. Air-dry soil was sieved to < 0.5 mm, washed three times with 0.01 M CaCl_2 , and dried and sieved again. Three subset samples of the washed soil were prepared as follows. Samples were mixed with amounts of $\text{Ca}(\text{OH})_2$ solution to adjust the soil pH (in 10 mM CaCl_2) to 7.0 and 7.6. The soils were equilibrated on a side-to-side shaker in the dark for 3 weeks, air-dried and re-sieved to < 0.5 mm.

Solutions of U in 10 mM CaCl_2 were made as follows. A stock solution (1000 mg U L^{-1}) was prepared by dissolving 0.42 g of uranyl nitrate hexahydrate (TAAB Laboratories equipment Ltd., Aldermaston, UK) in ultra-pure water adjusted to pH 3.8 to prevent U precipitation. Volumes of the stock solution were added to 10 mM CaCl_2 to make 0, 10, 12, 24, 36, 48, and 60 mg U L^{-1} working solutions.

Aliquots of each U solution (2.5 cm^3) were added to 1 g of the air-dry soils in either 15 cm^3 polypropylene centrifuge tubes (ambient CO_2) or 12 cm^3 glass tubes (elevated CO_2 pressure experiments). The tubes were capped with rubber septa, and, in half of them, the CO_2 pressure was adjusted by replacing the headspace air with 5% CO_2 in air by passing the gas through the tubes for 30 s at 1 L min^{-1} . The flow rate and injection time were predetermined by sampling the headspace and analysing by gas chromatography (GC). Changes in CO_2 pressure in the headspace were negligible over the 24 h of the sorption measurements.

The tubes were shaken end-over-end for 24 h at 20°C. In preliminary experiments, this was shown to be sufficient time to reach a stable pH and U concentration (Appendix B-1). After shaking, the suspension pHs were measured using a combination electrode (Microelectrodes, Inc., Bedford, USA). The headspace CO_2 pressures were measured by GC. The suspensions were then centrifuged (3500 RCF; 10 min) and

filtered through 0.45 µm filters, and U concentrations in the filtrates measured as follows.

Aliquots of the centrifugate were diluted with 0.14 M HNO₃ at 1:10 to reduce matrix effects, and stored at 4°C until analysis. Uranium was analysed as ²³⁸U isotope using an ICP-MS (PerkinElmer NexIon 350 D, Boston, MA, USA) with rf forward power 1600 W, and Ar gas flows of 1.2 L min⁻¹ (carrier gas). Solutions were aspirated by a SeaSpray glass nebuliser at a rate of 0.94 mL min⁻¹. The instrument was operated in standard mode (STD) with -1700 and 1400 V for analog and pulse stage voltage, respectively. Three replicate sub-samples were analysed per sample. Standards were prepared from a single element stock solution (1000 mg U L⁻¹, Claritas PPT Grade, SPEX CertiPrep) diluted with 0.14 M HNO₃ to prevent salt precipitation in the instrument. The ²³⁸U limit of detection was 20 ng L⁻¹. Quality control was done using solutions treated in the same way but without soil. The recovery was 90 % (RSD = 2.5 %).

The amounts of U sorbed were inferred from the amounts added less the amounts remaining in solution according to

$$C_S = C_{\text{initial}} - RC_L \quad (3-2)$$

where C_S is the concentration per unit mass of soil, C_{initial} is the initial concentration per unit mass of the dry soil, R is the soil solution volume to dry soil ratio, and C_L is the final concentration per unit solution volume.

3.2.3 Sorption kinetics

Sorption kinetics were measured in shaken suspensions as in Section 3.2.2 but over an extended period: 216 h, with 10 sampling times spread over the 216 h. The U addition was 6.30×10^{-4} mol kg⁻¹ which corresponds to the U addition in the diffusion experiments in Chapter 4, with three pHs and two CO₂ pressures in triplicates. Ten sets of tubes were prepared for each pHs and CO₂ pressure combination, and a complete set of tubes was analysed at each sampling, as described in Section 2.3.2. The pH was monitored in additional tubes for any significant changes.

3.2.4 Data analysis

The results of the shaken suspension experiments were expressed graphically using the software SigmaPlot 11.0 (Systat Software Inc, Chicago, IL, USA). The concentration of adsorbed U, C_S , was plotted against the concentration in solution, C_L , and the fits of alternative sorption equations (linear with constant K_D , Freundlich and Langmuir) were assessed for each pH-CO₂ pressure combination. The fits to the sorption equations were used to evaluate the soil U buffer power, $b = dC_L/dC$, and its dependence on U concentration, pH and CO₂ pressure. The buffer powers so determined were used to calculate diffusion coefficients from Equation 3-1 and hence concentration-distance profiles of U through the soil in the half-cell U diffusion experiments presented in Chapter 4, assuming a constant U diffusion coefficient for each soil pH and CO₂ pressure as indicated by the U buffer power at the initial soil U concentration. The relevant solution of the diffusion equation for a constant diffusion coefficient and the boundary conditions of the half-cell system is (from Equation (2-6) and Crank, 1975, Equation 2.14)

$$\frac{C}{C_1} = \frac{1}{2} \operatorname{erfc} \left(-\frac{x}{2\sqrt{Dt}} \right) \quad (3-3)$$

where C = concentration at distance x and C_1 = initial concentration in the half-cells with added U. The concentration-distance profiles so obtained were compared with the predictions of a more-exact model allowing for both the concentration- and time-dependence of adsorption and desorption, which is presented in Chapter 4.

The results for sorption kinetics were plotted as distribution coefficients, K_D , expressed as:

$$K_D = \frac{C_S}{C_L} \quad (3-4)$$

Results were plotted in SigmaPlot 11.0 (Systat Software Inc, Chicago, IL, USA), and statistics (one sample t-test for individual condition; ANOVA for inter-group analysis by Kruskal-Wallis one way analysis of variance on ranks and Tukey test all pair-wise multiple comparison) were performed with the same software. The Kruskal-Wallis test is suitable where the independent variable (i.e. the groups of U

concentrations at each pH and PCO_2 condition) but the dependent variable (i.e. U sorption) is not normally distributed (Longjian, 2018). The Tukey procedure may be used to determine which pairs of means have statistically significant difference (Driscoll, 1996) and therefore was used to compare the data sets at the same pH but different PCO_2 .

3.3 Results

3.3.1 Uranium speciation

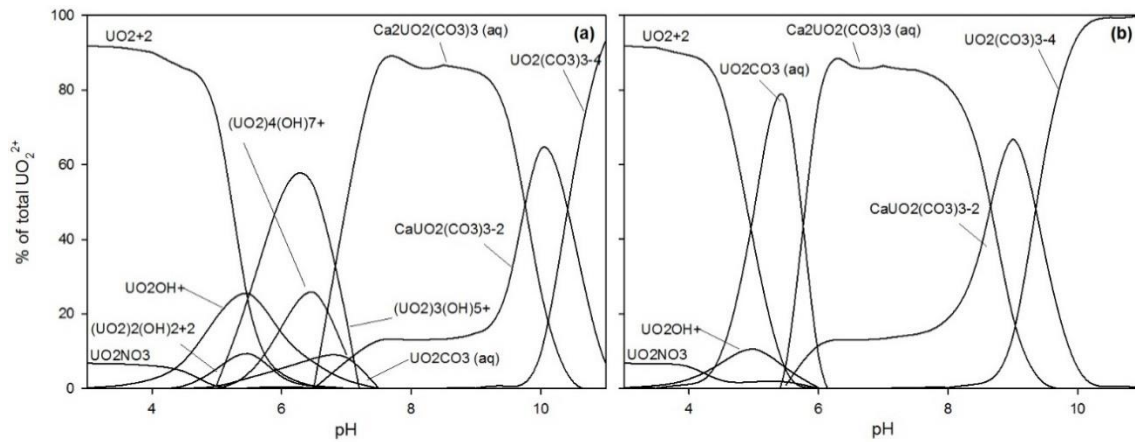


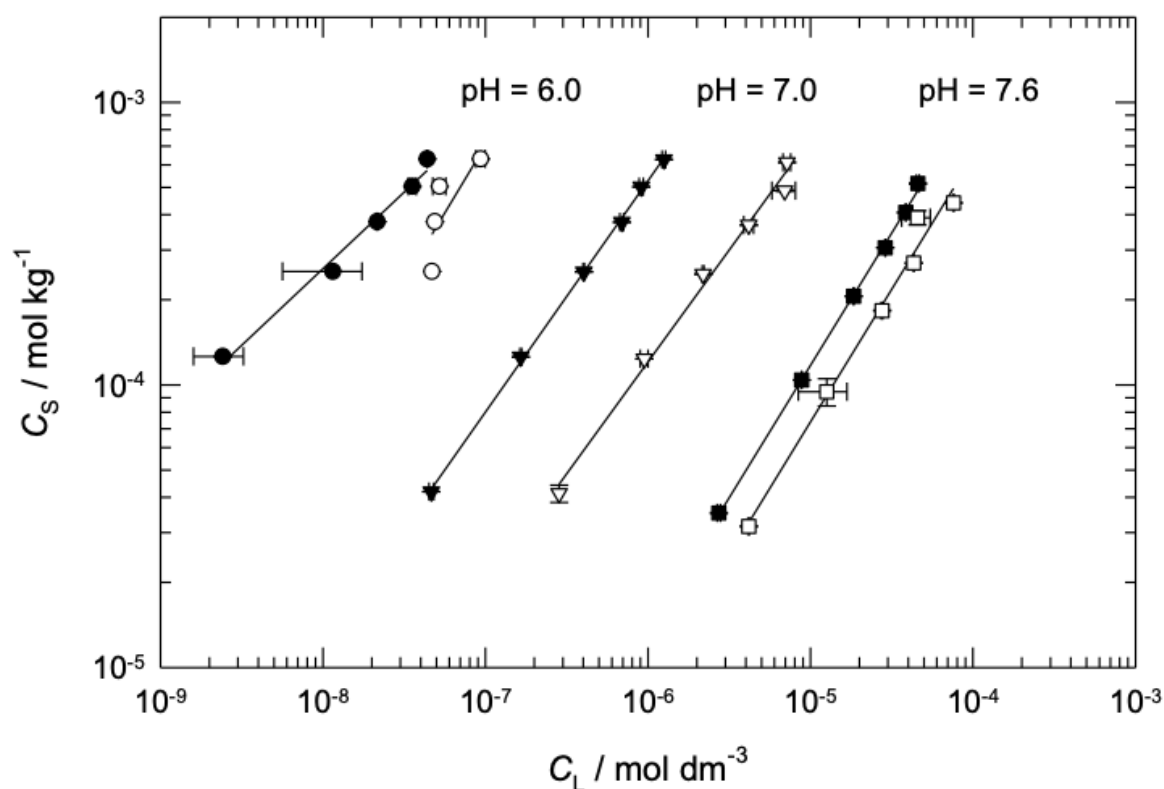
Figure 3-1 Distribution diagram of U species. The total dissolved U concentration 1×10^{-5} M. Ionic strength, $I = 0.03$ M, and $PCO_2 =$ **(a)** 0.04 kPa and **(b)** 5 kPa. Other components were: $[Ca^{2+}] = 0.01$ M, $[Cl^-] = 0.02$ M, and $[NO_3^-] = 1.26 \times 10^{-3}$ M. U species $< 2\%$ of total UO_2^{2+} are not shown.

Figure 3-1 shows distribution diagrams of dissolved U speciation. The free uranyl ion, UO_2^{2+} , was the predominant species at $pH < 5$, but other species dominated above $pH \approx 5.5$. The proportion of $UO_2^{2+}-OH^-$ species decreases with increasing PCO_2 as UO_2^{2+} -carbonate complexes increases.

The widely-observed bell-shaped relation between U sorption and pH is due to the combined effect of (a) decreasing dominance of UO_2^{2+} , which is strongly sorbed, with increasing pH, (b) increasing negative charge on soil surfaces with increasing pH, resulting in decreased sorption of anionic UO_2^{2+} -carbonate complexes. As the CO_2 pressure increases, the peak in sorption shifts to lower pH.

3.3.2 Soil-solution partitioning of U

The results in Figure 3-2 show that U sorption in shaken suspensions decreased with increasing pH (pH range 6.0-7.6) and CO₂ pressure (ambient vs 5 kPa). The results indicate almost complete adsorption (> 99 %) at pH 6.0 and pH 7.0 over the entire concentration range, and decrease in adsorption to about 80% at pH 7.6. Sorption gradually declined with increasing total U concentration in the dispersed soil.



	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
<i>m</i>	3.86	42.74	5.60	149.18	5.47	3.27
<i>n</i>	0.523	0.818	0.936	0.764	0.775	0.928
<i>r</i> ²	0.92	1.00	1.00	0.60	0.98	0.97

Figure 3-2 Uranium sorption measured in shaken soil suspensions. Closed symbols are at ambient CO₂ pressure; open symbols at CO₂ pressure = 5 kPa in air. Data are means ± SE; lines

are linear regression fits as in the table below. The lines are fits of the Freundlich-type equation, $C_S = mC_L^n$, with the coefficients m and n as shown in the table.

The U solubility further increased with higher CO₂ pressure. At elevated CO₂ pressure (5 kPa), U fraction in solution increased compared to ambient soil PCO₂ at given pH. At pH 6.0 and elevated CO₂ pressure, adsorption remained almost 100%. At pH 7.0, most U remained adsorbed but adsorption decreased from about 99% to $\approx 97\%$. At pH 7.6, adsorption decreased from $\approx 80\%$ to $\approx 70\%$, depending on the initial U concentration. At low U concentrations, the sorption remained almost the same, and the higher U concentrations showed increase in U solubility.

Sorption was successfully modelled with a Freundlich-type equation ($r^2 > 0.97$) except at pH 6.0 where the concentrations in solution were close to quantification limits. A Langmuir-type equation could not be fitted to the data (Appendix B-2.1), and nor could a linear equation with a constant K_D .

The m and n parameters from Freundlich isotherms were used to calculate the soil U buffer power, $b = dC/dC_L$ as follows. The total concentration in the soil is

$$C = \theta C_L + \rho C_S \quad (3-5)$$

where θ = soil volumetric moisture content and ρ = soil bulk density. Substituting $C_S = mnC_L^{n-1}$ and differentiating gives

$$b = \theta + \rho mnC_L^{n-1} \quad (3-6)$$

Figure 3-3 gives values of b so calculated across the concentration range in the shaken suspension measurements. It shows that the importance of concentration decreased with increasing concentration in this range, especially at high pH and elevated CO₂ pressure. The buffer power decreases by roughly an order of magnitude as pH increases from 6.0 to 7.0 and 7.6. At pH 7.6, the effect of CO₂ pressure is much reduced due to already high U-complexation with carbonate species at the lower CO₂ pressure.

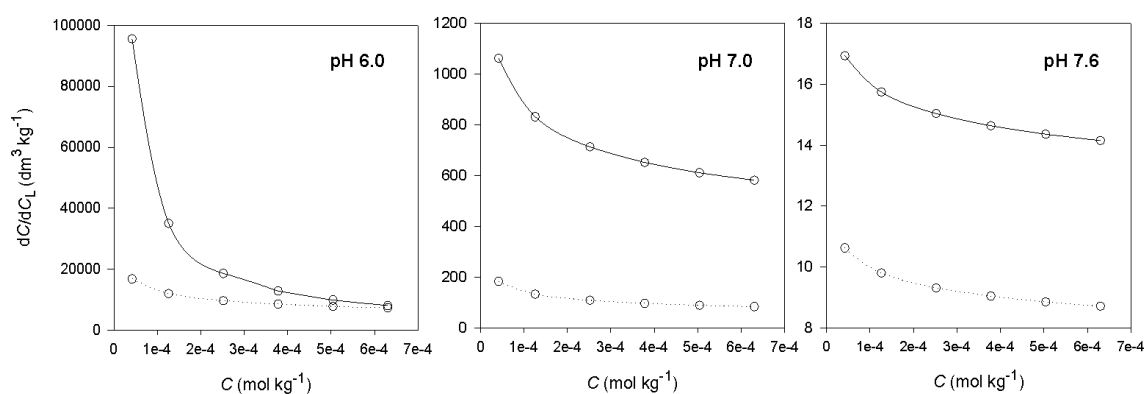


Figure 3-3 Concentration-dependence of soil U buffer power for the studied U concentration range. The buffer power was calculated with Equation (3-6) and the Freundlich coefficients fitted in Figure 3-2. The pH is indicated in each plot. The solid lines are for ambient CO₂ pressure; the dotted lines are for CO₂ pressure = 5 kPa.

3.3.3 Sorption kinetics

Figure 3-4 shows changes in U sorption over the 216 h shaking period at the three pHs and two CO₂ pressures, and single U addition ($6.3 \times 10^{-4} \text{ mol kg}^{-1}$). The results are plotted as K_D over time. The same trends with pH and CO₂ pressure as in Figure 3-2 are seen.

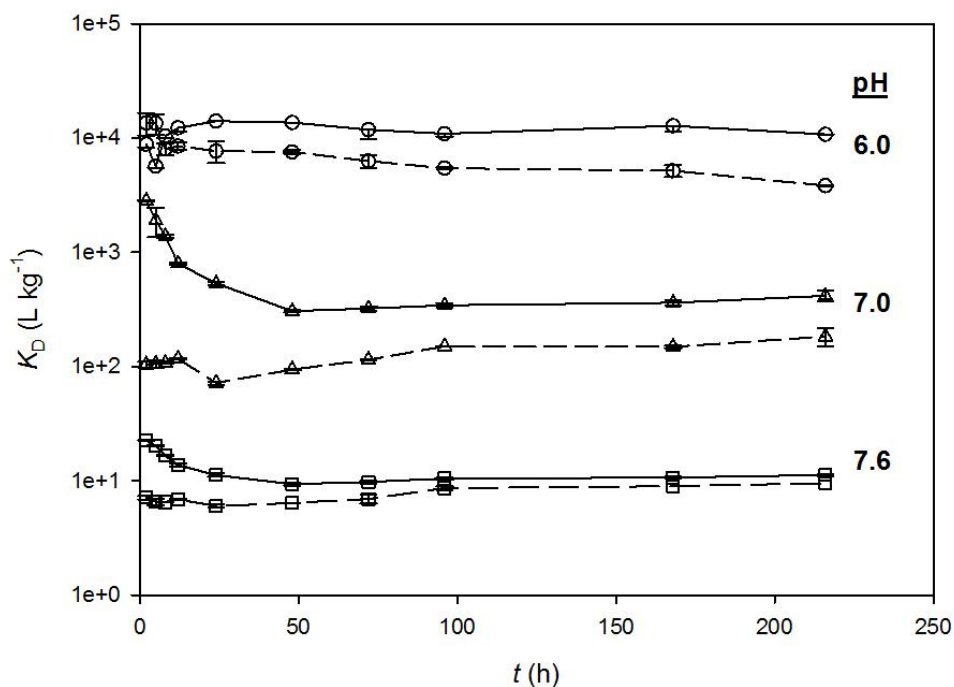


Figure 3-4 Sorption kinetics over 216 h equilibration measured in shaken suspensions. Uranium addition was $[U] = 6.3 \times 10^{-4} \text{ mol kg}^{-1}$. Solid lines represent initially ambient CO₂ pressure; dashed lines are for CO₂ pressure = 5 kPa.

At pH 6.0, an apparent equilibrium was achieved after 8 h but it was followed by a continuing gradual decline in sorption, which was found to be significant ($p < 0.05$). At pHs 7.0 and 7.6, there was a gradual increase in sorption over time at ambient CO₂ pressure, but at elevated CO₂ pressure, the initial rapid sorption was followed by a period of declining sorption, converging on the lines for ambient CO₂ pressure. The differences in sorption over time was confirmed by t-test for all conditions (Appendix B-3.1). However, the sorption kinetics could not be confirmed because of experimental limitations linked to changing CO₂ pressures over the shaking period, as discussed in Section 3.4.

Nevertheless, assuming equilibrium after 96 h at pH 7.0 and 7.6, the previously estimated buffer powers would have been over- and under- estimated, respectively, because of the insufficient shaking time (24 h). Based on the K_D in Figure 3-4, the over- and under- estimation could be expected to affect b -values mainly at pH 7.0 (especially at ambient CO_2) and only slightly at pH 7.6 where the sorption dynamics were less definite.

Changes in pH over time were found to be negligible (Appendix B-2.1). The ANOVA results for all conditions showed that the median K_D values of the groups differed between pH 6.0 and pH 7.6 only (for both CO_2 pressures), and between pH 6.0 and pH 7.0 under ambient CO_2 pressure. No significant differences were found between pH 7.0 and pH 7.6 under either CO_2 pressure (possibly due to the initial depression in K_D , resulting in a shift of the median value). Some group comparisons were inconclusive. The t-test and ANOVA results are given in Appendix B-3 (B-3 Statistical analysis).

3.3.4 Diffusion modelling

Table 3-2 compares the buffer powers calculated with the Freundlich parameters for the maximum and minimum U additions in the shaken suspensions, with buffer powers from the relations for U sorption in the model of U diffusion and reaction presented in Chapter 4. The buffer powers roughly agreed between the shaken suspension and the Chapter 4 model, and were within the K_D ranges for similar soils reported in the literature (EPA, 1999).

Table 3-1 Comparison of soil U buffer powers calculated from the shaken suspension data and Equation (3-6) with those derived from the diffusion and reaction model in Chapter 4.

	Buffer power, b ($\text{dm}^3 \text{ kg}^{-1}$)					
	Ambient air			5% CO_2 in air		
	pH			pH		
	6.0	7.0	7.6	6.0	7.0	7.6
<u>From shaken suspension</u>						
at $C = 6.3 \times 10^{-4} \text{ mol kg}^{-1}$	8058.8	582.0	14.2	7286.6	84.0	8.7
at $C = 6.2 \times 10^{-5} \text{ mol kg}^{-1}$	95580.5	1062.1	16.9	16813.2	183.4	10.6

From model in Chapter 4

at $C = 6.3 \times 10^{-4} \text{ mol kg}^{-1}$

6030

180.0

9.0

17900

129.0

5.0

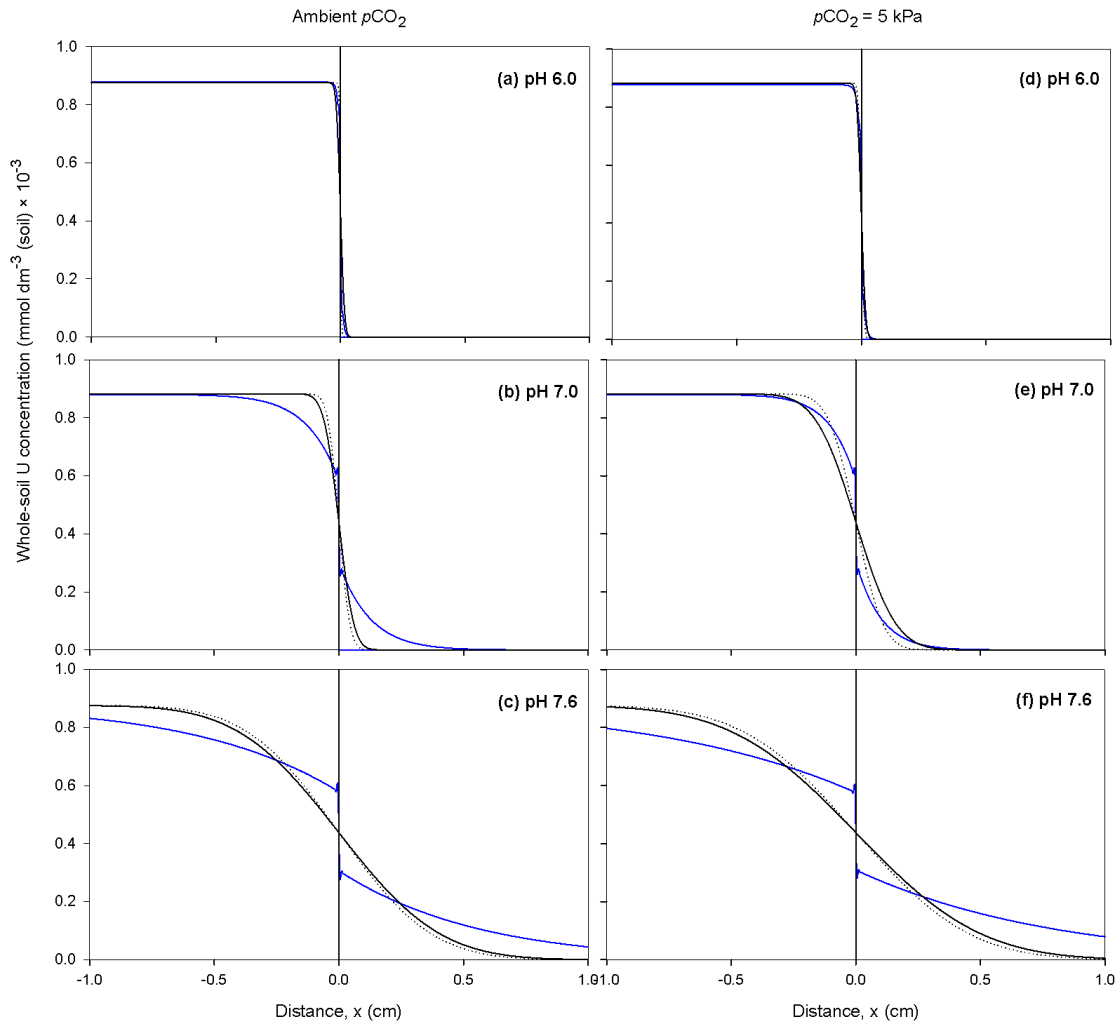


Figure 3-5 Predicted concentration-distance profiles of U after diffusion between two half-cells of soil, one initially with and the other without added U as in Chapter 4. **(a)–(c)** ambient PCO_2 (CO_2 pressure) and indicated pHs. **(d)–(e)** $PCO_2 = 5 \text{ kPa}$ and indicated pHs. The blue lines are calculated with the numerical model presented in Chapter 4, allowing for the kinetics of U adsorption and desorption. The black lines are calculated with the analytical solution to the appropriate form of the diffusion equation for a constant diffusion coefficient (Equation (3-3)), with D calculated using $(dC_L)/(dC_S)$ values in Table 3-2 (solid line is for $C = 6.3 \times 10^{-4} \text{ mol kg}^{-1}$ and the dotted line is for $C = 6.2 \times 10^{-5} \text{ mol kg}^{-1}$). The other model parameters are $\rho = 1.4 \text{ kg dm}^{-3}$, $\theta = 0.33$, $f = 0.39$, $t = 12 \text{ d}$.

Figure 3-5 shows calculated U concentration-distance profiles under the conditions of the experiments in Chapter 4 calculated with (1) Equation (3-3) and the buffer powers in Table 3-2, and (2) the model in Chapter 4, whose predictions agreed well with the measured profiles.

The results show there was not much difference between the predictions of Equation (3-3) with the buffer powers at different U concentrations, except at pH 7.0 and elevated CO₂ pressure. There was also not much difference between the predictions of Equation (3-3) and the more exact model at pH 6, where sorption was very high and there was little U diffusion. However, at pH 7.0 and 7.6 there were large differences between the two models in both the amounts of U transferred between the cells and the spreads of the respective depletion and accumulation profiles in the cells. The model with a constant diffusion coefficient (Equation (3-3)) predicts smooth sigmoidal curves, whereas the model from Chapter 4 allowing for slow sorption kinetics predicts a distinct discontinuity at the source-sink interface.

3.4 Discussion

3.4.1 Effect of pH and CO₂ pressure

The sorption experiments in shaken suspension confirmed that pH and CO₂ pressure were the principal factors controlling U soil-solution interchange. This is in agreement with all studies found across the literature (Catalano & Brown, 2005; Kumar *et al.*, 2014; Payne *et al.*, 2011; Uyuşur *et al.*, 2014, etc.). The general sorption trend was pH 6.0 (lower PCO₂) > pH 6.0 (higher PCO₂) > pH 7.0 (lower PCO₂) > pH 7.0 (higher PCO₂) > pH 7.6 (lower PCO₂) > pH 7.6 (higher PCO₂).

The decrease in sorption with pH and CO₂ pressure can be attributed to the complexation of U with carbonate ligands originating from dissolved CO₂. The dominant UO₂²⁺ and UO₂CO₃ species pH < 6.0 are replaced by Ca₂UO₂(CO₃)₃ and CaUO₂(CO₃)₃²⁻ at higher pH. Since Ca₂UO₂(CO₃)₃ is uncharged and so not sorbed, and CaUO₂(CO₃)₃²⁻ is anionic and so its sorption decreases as the soil surface negative charge increases with pH, net sorption decreases. Hence, U sorption is maximal at circum neutral pH and decreases under both acid and alkaline conditions.

This illustrates the potency of the pH-dependence of U sorption and its sensitivity to small pH changes. Root-induced changes in pH in the rhizosphere are often as much as 1 pH unit (Tinker & Nye, 2000). This together with the strong effect of increased CO₂ pressure shows the importance of correctly allowing for pH and CO₂ pressure in U transport and uptake models.

3.4.2 Effect of U concentration

The sorption of U was found to be concentration-dependent in the experimental soil, and well described with the Freundlich equation. However, the effect of concentration-dependence on overall diffusion in the soil was minor compared to the effects of pH and CO₂ pressure. Hence, ignoring the concentration-dependence of D in diffusion modelling was appropriate for this soil, though potentially not for others in which concentration-dependence may be more acute.

The concentration-dependence of U sorption undermines the use of constant K_D values to predict U mobility. K_D values are concentration-specific and their application to calculate diffusion coefficients can be erroneous if applied for other U concentrations and/or system conditions. Literature K_D values vary by orders of magnitude at similar U concentrations, depending on soil types and measurement conditions.

3.4.3 Sorption kinetics

The results of the sorption kinetics experiment suggest various types of slow reaction may have occurred over the studied period. Slow U adsorption reactions per se, leading to increased K_D over time, were only obviously apparent in the tubes at ambient CO₂ and pHs 7.0 and 7.6. Experimental limitations prevent firm conclusions. But various other slow processes may have occurred, masking slow adsorption reactions.

First there is the possibility of CO₂ accumulation in the tubes as a result of continuing soil respiration over the shaking period. The following simple calculation shows this may have been significant. A typical low soil respiration rate is 1 µg CO₂ g⁻¹ h⁻¹ (Rowell, 1994). There was 1 g of soil per tube and approx. 10 cm³ of head space. Therefore $1 \times 10^{-6} \times 216 \times 100 / 44$ mol CO₂ was produced per L of headspace over the 216 h of the experiments. Using the gas equation, with $R = 0.082 \text{ L atm K}^{-1} \text{ mol}^{-1}$ and T

= 273 K, gives an increase of CO₂ in the headspace of 0.012 L L⁻¹ or 1.2%. Unfortunately CO₂ in the headspace was not monitored over time. But this might account for the apparent decrease in sorption over time at pH 6.0 and ambient CO₂ pressure. But probably not the much greater decreases in sorption observed in the elevated CO₂ tubes.

A second process, which might account for decreasing sorption in the elevated CO₂ tubes, is precipitation of U-free carbonates, resulting in a lowering of the CO₂ pressure in the headspace. However, this seems unlikely as there were no pH changes in the suspensions over the shaking period. A more likely possibility is that there was a gradual leakage of CO₂ from the elevated CO₂ tubes. This would have caused a smaller pH change, but would have affected U sorption.

3.4.4 Diffusion modelling

The calculated concentration-distance profiles using Equation (3-3) with a constant diffusion coefficient and ignoring the time-dependency of sorption did not match those calculated with the more accurate model, which accurately predicts the profiles presented in Chapter 4. The calculations with Equation (3-3) mostly underestimated the diffusive flux of U through the soil, and failed to depict the observed shape of the concentration-distance profiles. The model of Boghi *et al.* (2018), described in Chapter 4, allows for the time-dependency of sorption in addition to the effects of pH, CO₂ pressure and U concentration. This model accurately predicted the diffusion profiles measured in Chapter 4.

This proves that, although attractive for its simplicity, the shaken suspension approach is insufficient for the modelling purposes of U diffusion on the time scale relevant to root uptake. Hence U phytoavailability in soil may be seriously underestimated by such measurements and empirical models based on them. More sophisticated mechanistic modelling is required.

The underlying sorption mechanisms are still incompletely understood. The rate-limiting steps are likely to involve slow access to or from sorption sites within soil aggregates by diffusion in the intra-aggregate pore space, rather than slow chemical

reactions on soil surfaces (Nye & Staunton, 1994; Ptashnyk *et al.*, 2010). Further progress will require experimental techniques for exploring such processes.

3.5 Conclusions

The null hypothesis, given in Section 2.1.1, that U diffusion can be predicted without allowing for the concentration- and time-dependence of sorption, is rejected. The concentration-dependence has less importance than the dependence of sorption on pH and CO₂ pressure. But the time-dependence is marked and ignoring it leads to large errors in diffusion calculations. The specific findings were:

- Uranium sorption was pH-dependent with a maximum near pH 6.0, and pH was the most important factor in U solid-solution partitioning.
- Sorption also depended on CO₂ partial pressure and U solubility increased with CO₂ partial pressure and pH due to complexation with dissolved carbonate ligands.
- The experiments on sorption kinetics were inconclusive due to experimental limitations. The results indicated continuous sorption reactions which could be attributed to accumulation of respired CO₂ followed by U-carbonate complexation in solution, especially at pH 7.0 and ‘ambient’ CO₂ pressure.
- Calculations of U diffusion that ignored the time-dependency of sorption did not correctly predict U diffusion in soil, as demonstrated by poor agreement with U concentration-distance profiles calculated with a more- complete model of U diffusion and reaction, which is presented in Chapter 4.
- Although sorption parameters from shaken suspensions alone are not suitable for modelling U diffusion towards a root, they can help to constrain parameters for more sophisticated models.

CHAPTER FOUR

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

Foreword

This chapter reproduces a manuscript that, at the time of writing, is in review for publication in the *European Journal of Soil Science*. The manuscript was submitted on 27 November 2018. The manuscript describes the experimental testing of a model of U diffusion and reaction in soil. The model was developed by Dr Boghi and Profs Kirk and Roose based on an earlier model they developed, described in Boghi *et al.* (2018). All the experimental work was carried out and analysed by myself as part of this thesis. The manuscript was written by Prof. Kirk with contributions from myself and the other co-authors.

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 and soil biota, which operates over much smaller time and distance scales. We develop and test 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 are compared with experimentally-measured concentration-distance profiles of U in soils adjusted to different pHs and CO₂ pressures. Excellent agreement between observed and predicted profiles is obtained using model input parameters measured or otherwise estimated independent of the concentration-distance profiles, showing that the model is a correct description of the system and all important processes are 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 develop a model of U diffusion and reaction in soil on scales relevant to uptake by plant roots.
- We test the model against measured diffusion profiles and obtain 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.

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 via uptake from soil by plants. 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 length 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 rigorously test it against experiments. In this paper we provide such a rigorous testing.

Simple calculations show that uptake rates 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 gives such calculations for U uptake by ryegrass in a range of soils, based on data of Duquène *et al.* (2010). This implies 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, down which U diffuses. Uranium uptake is enhanced where roots are colonized by mycorrhizal fungi, though 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 – from where it is taken up 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 relationship is bell-shaped with a

peak around neutral pH but shifting to lower pH with increasing CO₂ pressure (Davis *et al.*, 2004; Geckeis *et al.*, 2013; Mitchell *et al.*, 2013). Hence diffusion through the soil solution to absorbing roots may be sensitive to the changes in rhizosphere pH and CO₂ 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; Eagling *et al.*, 2013; Stoliker *et al.*, 2013). Our model (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 CO₂ 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 CO₂ pressures in the ranges in which U mobility is expected to be high. We compare 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:

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

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

$$D = D_L \theta f \frac{dC_L}{dC} \quad (2)$$

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 Boghi *et al.* (2018). The boundary conditions are

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

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: one that exchanges effectively instantaneously with U species in the soil solution, and one that exchanges more slowly. Hence

$$C = \theta C_L + \rho (C_{S1} + C_{S2}) \quad (4)$$

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,

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

For the fast-reacting U,

$$\frac{\partial C_{S1}}{\partial t} = \frac{\partial C_{S1}}{\partial C_L} \frac{\partial C_L}{\partial t} = b \frac{\partial C_L}{\partial t} \quad (6)$$

where the derivative b is the buffer power for the solid-solution distribution of fast-reacting U, which is a function of pH and CO₂ 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):

$$\frac{dC_{S2}}{dt} = k_1 C_{S1} - k_2 C_{S2} \quad (7)$$

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

$$D \frac{\partial C}{\partial x} = D \frac{\partial C}{\partial C_L} \frac{\partial C_L}{\partial x} = D_L \theta f \frac{\partial C_L}{\partial x}. \quad (8)$$

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

$$(\theta + \rho b) \frac{\partial C_L}{\partial t} = \frac{\partial}{\partial x} \left(D_L \theta f \frac{\partial C_L}{\partial x} \right) - \rho (k_1 C_{S1} - k_2 C_{S2}) \quad (9)$$

Equations for U speciation and fast sorption. In our experimental system, the soil contains Ca²⁺, H⁺, H₂CO₃, HCO₃⁻, CO₃²⁻, Cl⁻ and L⁻ (representing organic ligands) in the soil solution and Ca²⁺ in the soil exchange complex, in addition to U. The important U species are UO₂²⁺, UO₂CO₃, Ca₂UO₂(CO₃)₃, CaUO₂(CO₃)₃²⁻ and UO₂L⁺. The total concentration of U species in the soil solution is therefore:

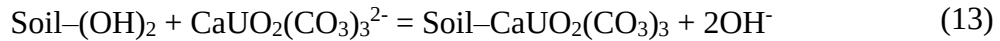
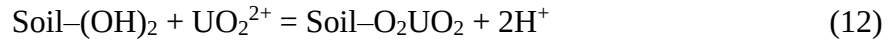
$$C_L = [UO_2^{2+}]_L + [UO_2CO_3]_L + [Ca_2UO_2(CO_3)_3]_L + [CaUO_2(CO_3)_3^{2-}]_L + [UO_2L^+]_L = [UO_2^{2+}]_L \left\{ 1 + K_{UO_2CO_3} [CO_3^{2-}]_L + K_{Ca_2UO_2(CO_3)_3} [Ca^{2+}]_L^2 [CO_3^{2-}]_L^3 + K_{CaUO_2(CO_3)_3^{2-}} [Ca^{2+}]_L [CO_3^{2-}]_L^3 + K_{UO_2L^+} [L^-]_L \right\} \quad (10)$$

where the K terms are the respective conditional equilibrium constants adjusted for activity coefficients. The unknowns in Equation (10) are $[\text{UO}_2^{2+}]_L$, $[\text{CO}_3^{2-}]_L$ and $[\text{Ca}^{2+}]_L$. $[\text{CO}_3^{2-}]_L$ is defined by the pH and CO_2 pressure. $[\text{Ca}^{2+}]_L$ is defined by the electrical neutrality condition:

$$2[\text{Ca}^{2+}]_L + 2[\text{UO}_2^{2+}]_L + [\text{UO}_2\text{L}^+]_L + [\text{H}^+]_L = [\text{Cl}^-]_L + [\text{HCO}_3^-]_L + [\text{L}^-]_L + 2[\text{CaUO}_2(\text{CO}_3)_3^{2-}]_L \quad (11)$$

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) use 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:



and the corresponding two mass-action equilibrium equations:

$$\frac{C_{S11}[\text{H}^+]_L^2}{X_{S1}[\text{UO}_2^{2+}]_L} = K_{S,\text{UO}_2^{2+}} \quad (14)$$

$$\frac{C_{S12}[\text{OH}^-]_L^2}{X_{S1}[\text{CaUO}_2(\text{CO}_3)_3^{2-}]_L} = K_{S,\text{CaUO}_2(\text{CO}_3)_3^{2-}} \quad (15)$$

where $C_{S11} = [\text{Soil}-\text{O}_2\text{UO}_2]_S$, $C_{S12} = [\text{Soil}-\text{CaUO}_2(\text{CO}_3)_3]_S$, $X_{S1} = [\text{Soil}-(\text{OH})_2]_S$, 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 CO₂ 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, CO₂ 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 optimise 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 $E = \frac{1}{N} \sum_{i=1}^N |C_i^{\text{measured}} - C_i^{\text{modelled}}|$ for the N experimental treatments $\times$ replicates.

Bromide diffusion

We measured the diffusion of Br⁻ ions in our experimental system to confirm 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 the tortuosity of the pore space, and hence 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^- and subscripts 0 and 1 refer to the initial sink and source cells, respectively. For a non-adsorbed solute, $C = \theta C_L$ and hence 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

$$\begin{aligned} C = C_1 \quad x = 0 \quad C = C_0 \quad x > 0 \quad t = 0 \\ C = C_0 \quad x = \infty \quad t \geq 0 \end{aligned} \quad (18)$$

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)

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

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. 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) = 10.2 $\text{cmol}_c \text{ kg}^{-1}$, organic C content = 30.2 g kg^{-1} , clay content =

145 g kg⁻¹, silt content = 328 g kg⁻¹. The soil was washed three times with 10 mM CaCl₂ at a solution to soil ratio of 5:1, 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 ²³⁵U-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 CaCl₂) 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 $\approx 1.4 \text{ kg dm}^{-3}$. 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-up from below with 10 mM CaCl₂ so that entrapped air was displaced, and it was then placed on a pressure plate for 10 d 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 °C 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% CO₂ in air through the box at 0.05 L min⁻¹. The P_{CO_2} in the soil air was measured in cells incubated in this way (next section). The values were $P_{\text{CO}_2} = 1.3 \pm 0.1$ and 6.5 ± 0.1 kPa in the ambient and elevated CO₂ 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 d, the cells were separated, frozen in liquid nitrogen and sectioned at approx. 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 h and then U extracted by placing them in 8 mL of aqua regia (3:1 concentrated HCl:HNO₃) 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 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, with rf forward power 1540 W and reflected power 1 W, and Ar gas flows of 0.81 L min⁻¹ and 0.19 L min⁻¹ for carrier and makeup flows, respectively. Solutions were aspirated by a micro-mist nebuliser at a rate of 1.2 mL min⁻¹. The instrument was operated in spectrum acquisition mode. Three replicate samples were analysed per sample. Standards were prepared from a single element stock solution (1000 µg U L⁻¹, PlasmaCal, SPE Science) 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) diluted 100-fold to give 100 µg U L⁻¹. The extraction efficiency of this method was close to 100% as measured by digesting a certified reference soil (IRMM; ERM-CC141).

CO₂ 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% CO₂ in air through the box at 0.05 L min⁻¹. After 48 h, the cells were sliced axially into five sections and dissolved CO₂ in the soil solution measured as follows. Approx. 5 g subsamples of each section were placed in centrifuge filtration units (Millipore Ultrafree Centrifugal Filter Device with a 0.22 µm membrane), capped and then centrifuged at 3,500 *g* for 15 min, collecting the soil solution. Dissolved CO₂ concentrations in the soil solutions were measured within a

few minutes of collection using a micro-electrode (MI-720 electrode, Microelectrodes Inc, USA). Preliminary experiments showed the solution pH did not change over the few minutes between sampling and analysis, indicating no degassing of dissolved CO₂. Calibration solutions (0.25–10 % CO₂) were prepared by dissolving NaHCO₃ in CO₂-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 CaBr₂ in 10 mM CaCl₂ when initially wetting-up 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 °C for 4 h. The cells were then sectioned as above and Br concentrations analysed by shaking the sections end-over-end for 30 min with 0.01 M CaCl₂ at 1:10 soil:solution ratio, centrifuging the resulting suspensions at 4,000 *g* for 10 min, 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 CaBr₂ in 10 mM CaCl₂ against one end of the cell. After 5 min the membrane was removed, and the cell was incubated at 20 °C for 2 h 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) fitted iteratively, progressively rejecting data far from $x = 0$ until all the remaining data agreed with the fitted values to within two standard deviations (Matsullat *et al.*, 2009). The fits were made using 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 CaCl₂ were made using uranyl nitrate. Aliquots (2.5 cm³) of the solutions were added to 1 g of air-dry soils, prepared as under *Uranium diffusion*, in 12 cm³ glass tubes. The tubes were capped with

gas-tight rubber septa, and, in half of them, the headspace air was displaced with 5% CO₂ in air by passing the gas through the tubes at 1 L min⁻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 CO₂ pressure for the 24-h duration of the sorption measurements. The tubes were shaken end-over-end for 24 h at 20 °C, after which the suspension pHs were measured with a combination electrode. The suspensions were centrifuged at 3,500 *g* 10 min 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 $x^2/4D_L t$ for of a pulse application of Br⁻ ions on the soil in accordance with Equation (19). From the slope the diffusion impedance factor under the conditions of the main experiments was $f = 0.39$ (sd = 0.00, $n = 2$). 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 good 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. The values of the equilibrium constants for solution speciation were taken from MINTEQA (Gustafsson, 2013), adjusted for ionic strength using the Davies equation. From the experimental set up, $\rho = 1.4 \pm 0.01$ kg dm⁻³ (soil), $\theta = 0.35 \pm 0.01$, $f = 0.39$ (last section), $[Cl^-]_L = 20$ mM, $[L^-]_L = 0.1$ mM, pH = 6.0, 7.0 or 7.6 and $P_{CO_2} = 1.3$ or 6.5 kPa. We set $S_1 = 5$ 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 ($\equiv 0.63$ mmol U kg⁻¹). The following parameters were fitted to the data: $K_{s,UO_2^{2+}} = 2.30 \times 10^{-3}$ mol dm⁻³ (solution),

$K_{\text{S,CaUO}_2(\text{CO}_3)_3} = 7.34 \times 10^{19} \text{ mol dm}^{-3} \text{ (solution)}$, $k_1 = 6.95 \times 10^{-6} \text{ s}^{-1}$ and $k_2 = 9.39 \times 10^{-7} \text{ s}^{-1}$.

The apparent values of the buffer power $b = dC_{\text{S1}}/dC_{\text{L}}$ are 6.03×10^4 , 180 and $5 \text{ dm}^3 \text{ kg}^{-1}$ at pH 6.0, 7.0 and 7.6 and $= 1.3 \text{ kPa}$, respectively, and 1.79×10^4 , 129 and $3 \text{ dm}^3 \text{ kg}^{-1}$ at $P_{\text{CO}_2} = 6.5 \text{ kPa}$, respectively (Figure 3). The magnitudes of these values and their trends with pH and P_{CO_2} broadly agree with the values obtained in shaken soil suspensions (Figure 4). These are $b = dC_{\text{S}}/dC_{\text{L}} = nmC_{\text{L}}^{n-1}$ (where m and n are Freundlich coefficients fitted to the data) $= 5.74 \times 10^3$, 428 and $10 \text{ dm}^3 \text{ kg}^{-1}$ at pH 6.0, 7.0 and 7.6 and ambient P_{CO_2} , respectively, and $5.21 \times 10^3 \text{ dm}^3 \text{ kg}^{-1}$, 60 and $6 \text{ dm}^3 \text{ kg}^{-1}$ at $P_{\text{CO}_2} = 6.5 \text{ kPa}$, respectively.

At equilibrium, $dC_{\text{S2}}/dt = 0$ and from Equation (7), $k_1C_{\text{S1}} = k_2C_{\text{S2}}$. Therefore, since $\rho(C_{\text{S1}} + C_{\text{S2}}) \gg \theta C_{\text{L}}$ (equilibrium $C_{\text{L}} = 0.06$, 1.2 and $48.2 \text{ } \mu\text{M}$ at pH = 6.0, 7.0 and 7.6 and $P_{\text{CO}_2} = 1.3 \text{ kPa}$, and 0.09, 8.0 and $69.9 \text{ } \mu\text{M}$ at $P_{\text{CO}_2} = 6.5 \text{ kPa}$), the fraction of total U that is slowly reacting is $C_{\text{S2}}/(C_{\text{S1}} + C_{\text{S2}}) = 1/(1 + k_2/k_1) = 0.88$, 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 (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 approximately 5-fold difference in P_{CO_2} between the experimental treatments caused roughly a 2.8-fold increase in U transferred at pH 7.0 and a 1.8-fold increase difference at pH 7.6.

A striking finding is 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) shows how

such an interface resistance is expected to produce discontinuities in concentration-distance profiles, and that the effect will increase as Dt decreases (Crank, 1975, Fig. 3.7). The value of Dt for Br^- diffusion in our experimental system ($= 1.1 \times 10^{-3} \text{ dm}^2$) was comparable to that for U diffusion at pH 7.6 ($= 0.8$ and $1.4 \times 10^{-3} \text{ dm}^2$ at $P_{\text{CO}_2} = 1.3$ and 6.5 kPa , respectively). So the smooth profiles we obtained for Br^- diffusion (Figures 2B and S1), and the close agreement of these profiles with theory, show 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. Since there is no interface resistance, the concentrations of U in the soil solution 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 $t_{1/2} = \ln 2/k_2 = 8.5 \text{ d}$. Boghi *et al.* (2018) showed that slow equilibration will increasingly affect rates of U diffusion in soil for $k_2 < 10^{-6} \text{ s}^{-1}$ (i.e. $t_{1/2} > 8 \text{ d}$). Such rates are reported in the literature (Braithwaite *et al.*, 1997; Qafoku *et al.*, 2005; Handley-Sidhu *et al.*, 2009; Eagling *et al.*, 2013). However, the published measurements are 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 only slowly accessed 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} as they affect both U speciation in solution and the soil surface charge. Boghi *et al.* (2018) only considered sorption of the uranyl cation, UO_2^{2+} , by the soil solid (Equation 12). However at the high pH and

CO₂ pressures of our experimental system, we find it is necessary to also allow for sorption of the CaUO₂(CO₃)₃²⁻ 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 are 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 $K_{\text{S,CaUO}_2(\text{CO}_3)_3^{2-}}$ but not $K_{\text{S,UO}_2^{2+}}$ because UO₂²⁺ is unimportant compared with CaUO₂(CO₃)₃²⁻. It also shows 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 as this affects both microbial activity and the escape of respiratory CO₂ by diffusion in the soil air. Hence values are generally at least an order of magnitude above atmospheric P_{CO_2} . Likewise the predicted flux decreases as k_2 decreases below the standard value, but is not sensitive to increases above the standard value. Changes in k_1 at constant k_2 do not have much effect. As k_1 increases from 0.1 to 10 × the standard value, the equilibrium distribution of $U = C_{\text{S}2} / (C_{\text{S}1} + C_{\text{S}2}) = 1 / (1 + k_2 / k_1)$ increases from 0.43 to 0.99. However, increases in k_1 will not much influence net adsorption – and hence the flux across $x = 0$ – if $k_1 C_{\text{S}1} \ll k_2 C_{\text{S}2}$.

Implications for U uptake by plants

We have shown that U transport is slow at pH < 6 but increases steeply at pH > 6. Boghi *et al.* (2018) showed that root-induced pH changes driven by the plant's N nutrition are likely to be important in this pH range. Ammonium (NH₄⁺) fed plants tend to acidify their rhizosphere, and this will tend to diminish U uptake. Whereas nitrate (NO₃⁻) fed plants make their rhizosphere more alkaline, and this will increase U uptake. The pH change is often as much as one unit, but is sensitive to the initial pH and CO₂ 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 decreasing the diffusive flux to a sink such as a plant root. An implication 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, as these affect the spread of depletion profiles.

Supporting information

A. Maximum U influx into roots due to mass flow.

B. Further results

1. Measured and calculated concentration-distance profiles of Br for two replicates.
2. Measured and calculated concentration-distance profiles of U for all experimental treatments and replicates.

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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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	$\text{dm}^2 \text{s}^{-1}$
D_L	diffusion coefficient in free solution	$\text{dm}^2 \text{s}^{-1}$
f	diffusion impedance factor	
$[\text{ion}]_L$	concentration of ion in the soil solution where ion = U species, Ca^{2+} , L^- , Cl^-	mol dm^{-3} (solution)
$K_{\text{S, UO}_2^{2+}}$	equilibrium constant for fast sorption of UO_2^{2+} (Equation 14)	mol dm^{-3} (solution)
$K_{\text{S, CaUO}_2(\text{CO}_3)_3^{2-}}$	equilibrium constant for fast sorption of $\text{CaUO}_2(\text{CO}_3)_3^{2-}$ (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)

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

pH	U transferred (mol $\times 10^{-7}$)			
	$P_{\text{CO}_2} = 1.3 \text{ kPa}$		$P_{\text{CO}_2} = 6.5 \text{ kPa}$	
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

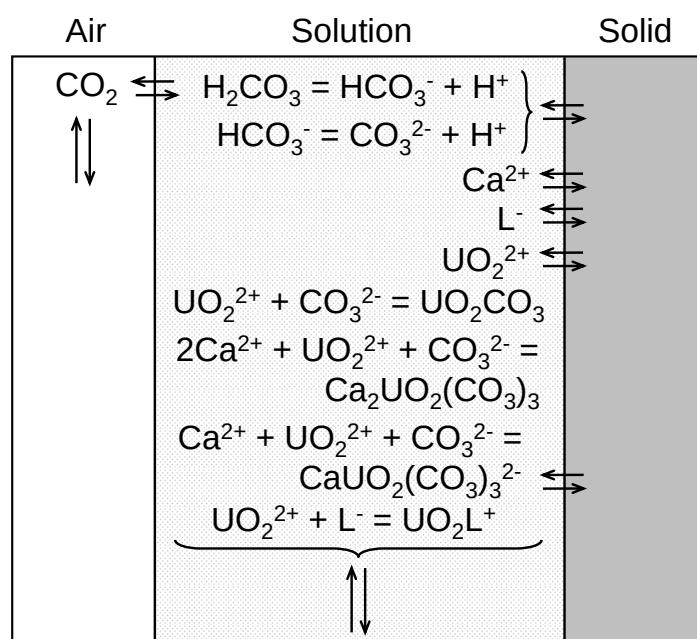


Figure 1 Speciation and sorption reactions controlling uranium diffusion in soil. Horizontal arrows indicate air-solution and solid-solution interchanges; vertical arrows indicate diffusion in the soil air and solution. Uranium species can diffuse in the soil solution but only very slowly in the soil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

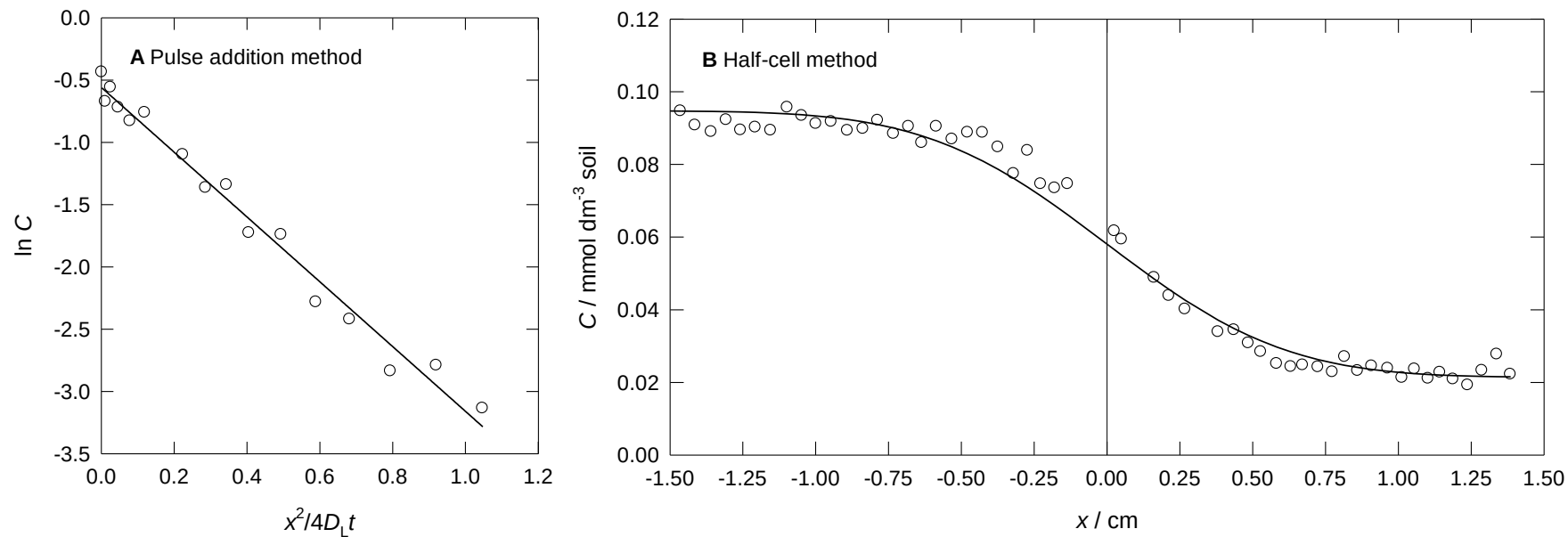


Figure 2 Concentration-distance profiles for Br⁻ diffusion in the experimental soil under the conditions of the main experiment. A For a pulse addition of Br⁻ on the surface of a soil column ($x = 0$); the points are measured data and the line is the fit to Equation (19) giving $f = 0.39$. B For two 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, $\rho = 1.42 \text{ kg dm}^{-3}$; volumetric moisture content, $\theta = 0.36$; $D_L = 2.0 \times 10^{-7} \text{ dm}^2 \text{ s}^{-1}$.

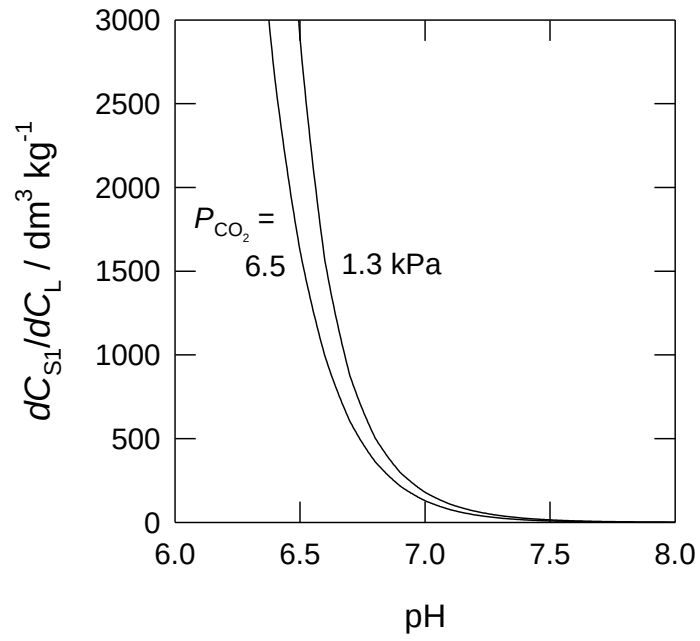
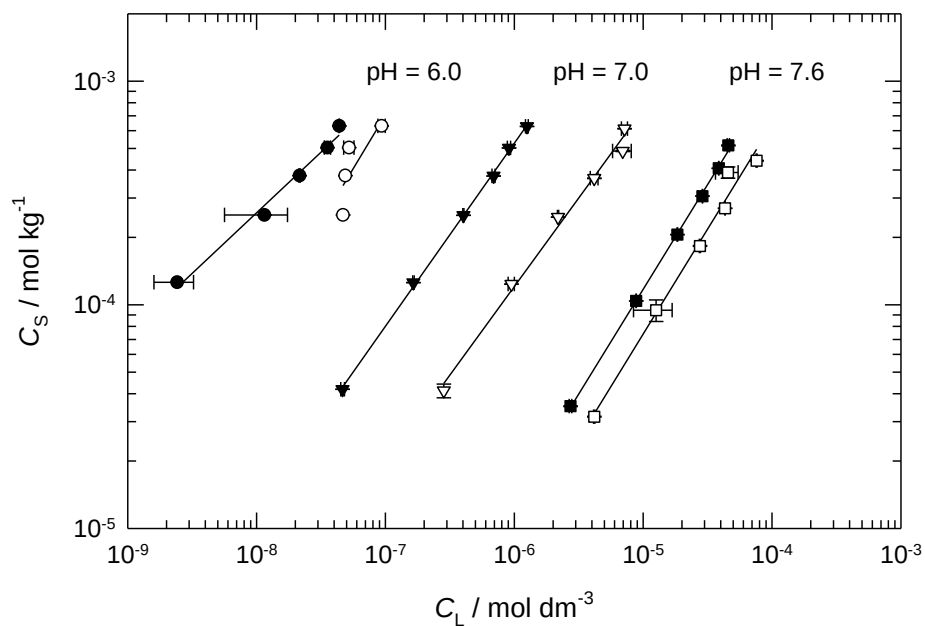


Figure 3 Effect of pH and P_{CO_2} on the buffer power $b = dC_{s1}/dC_L$ for fast U sorption.



	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
<i>m</i>	3.86	43.74	5.60	149.18	5.47	3.27
<i>n</i>	0.523	0.818	0.936	0.764	0.775	0.928
<i>r</i> ²	0.92	1.00	1.00	0.60	0.98	0.97

Figure 4 Uranium sorption measured in shaken soil suspensions. Closed symbols are at ambient CO₂ pressure; open symbols at 5% CO₂ in air. Data are means $\pm$ SE; lines are fits of the data to $C_S = mC_L^n$ with the coefficients *m* and *n* as shown in the table.

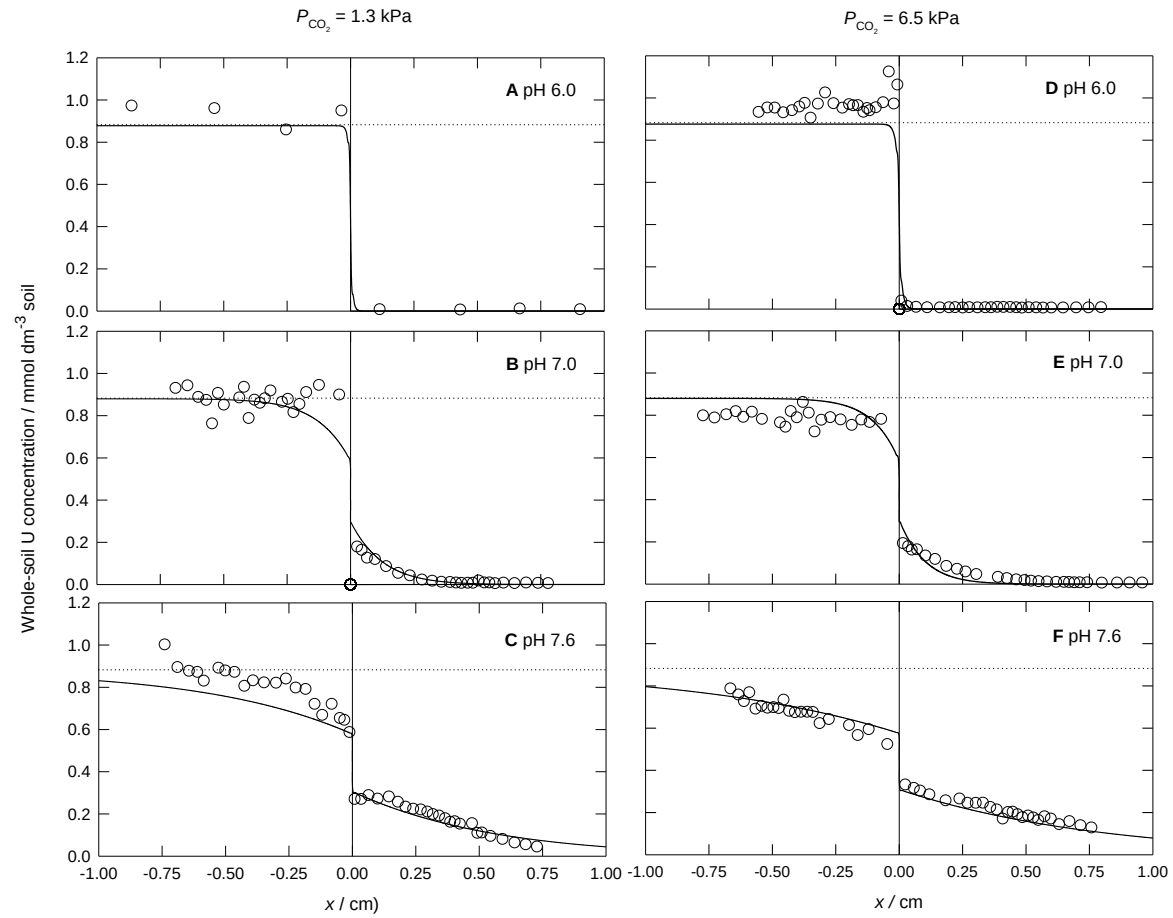


Figure 5 Concentration-distance profiles of U after diffusion between two half-cells of soil, one initially with and the other without added U. Points are observed data; solid lines are calculated with the model; dashed lines are added U. **A–C** P_{CO_2} (CO_2 pressure) = 1.3 kPa and indicated pHs. **D–E** P_{CO_2} = 6.5 kPa and indicated pHs.

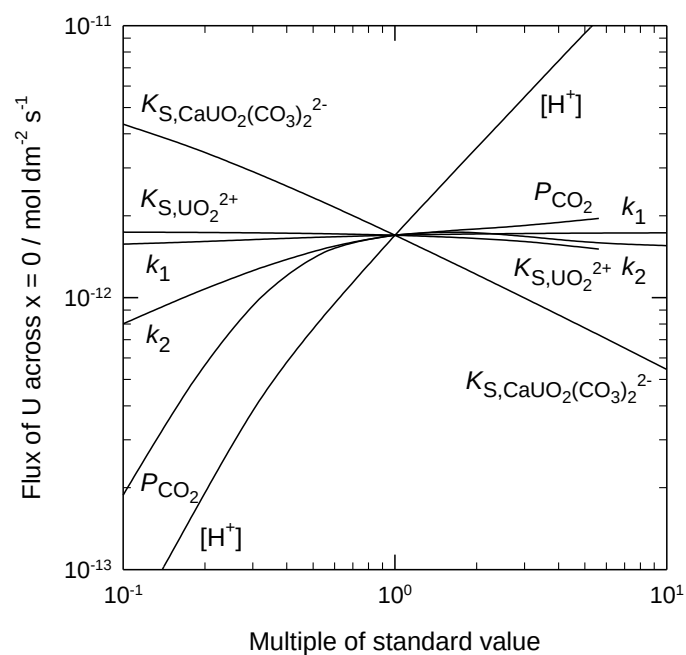


Figure 6 Sensitivity of the model to its input parameters. Each of the indicated parameters is varied in turn with the other parameters at their standard values. pH = 7=0; other standard parameter values as for Figure 4. $K_{S,UO_2^{2+}}$, $K_{S,CaUO_2(CO_3)_3^{2-}}$ = equilibrium constants for sorption of UO_2^{2+} , $CaUO_2(CO_3)_3^{2-}$; k_1 , k_2 = forward, backward rate constants for slow U sorption; P_{CO_2} = CO_2 pressure in the soil air; $[H^+]$ = initial H^+ concentration in the soil solution.

CHAPTER FIVE

General discussion and conclusions

The overall aim of the research reported here was to improve understanding of the transport processes controlling U uptake by plant roots. It was part of a wider research project on the fate and behaviour of long-lived radionuclides in the near-surface environment: the Lo-Rise project managed by the University of Manchester. The focus was on diffusive transport, convective transport being negligible at the typically small concentrations of U in soil solutions and typical rates of water inflow into roots (Chapter 4, Table S1). A further focus was on the effects of soil pH and CO₂ pressure on U diffusion, because these are known to be altered by root-induced changes in the rhizosphere and to strongly influence U mobility in soils (Mitchell *et al.*, 2013; Boghi *et al.*, 2018). The broad approach was to understand the above processes well enough to develop a predictive mathematical model of them, and to test the model against experimental measurements with the model parameters measured as far as possible independently. The main work was the development and execution of experimental methods for these purposes. The mathematical model was developed in another part of the Lo-Rise project.

In order to quantify U diffusion in soil, the methodology followed well-established theory of solute diffusion in soil, as set out in Tinker & Nye (2000). The essence of this is that the diffusion coefficient of a solute in soil is given by $D = D_L \theta f(dC_L/dC)$ where θf represents the soil moisture status and the tortuosity of the diffusion pathway through the soil solution, and the derivative dC_L/dC is the inverse of the buffer power, which represents the interchange of the solute between the soil solution and soil solid. Knowledge of D allows calculation of rates of diffusion with appropriate solutions of the diffusion equation. In principle the U buffer power, and hence D , depends on the concentration of U, the pH, the CO₂ pressure and time (Boghi *et al.*, 2018). In the thesis, methods were developed for measuring these dependencies and the other components of D , and for measuring concentration-distance profiles of U through soil with which to test diffusion models.

5.1 Measurement of solute diffusion in soil

Two methods for measuring solute diffusion in soil are compared in Chapter 2: the ‘pulse-addition’ method, in which a trace amount of solute is placed on one end of a soil column and the resulting concentration-distance profile through the soil is determined; and the ‘half-cell’ method, in which two columns of soil containing different concentrations of the solute are placed in contact and the resulting concentration-distance profiles in each cell is determined. The comparison was simplified by considering the counter-diffusion of non-adsorbed Br^- ions against Cl^- . This reduced the components of D to just D_L and θ , which were known, and f , which could therefore be obtained from the results. The pulse-addition is considered the preferred method for measuring diffusion coefficients of non-adsorbed solutes with constant diffusion coefficients, because the relevant solution of the diffusion equation has a particularly simple form (Pinner & Nye, 1982). Whereas the half-cell method has the advantage that, for sorbed solutes, it can provide information on the concentration-dependence of D and on differences between desorption in the source cell and adsorption in the sink cell side (Olesen *et al.*, 2001).

The results of the comparison showed that the Br^- concentration-distance profiles obtained with the half-cell method could be reliably predicted using the appropriate solution of the diffusion equation and the value of D obtained with the pulse-addition method. However, the reverse did not apply: the profiles obtained with the pulse method were not reliably predicted with the value of f obtained from the half-cell results. This indicates the relative sensitivities of the two methods to D , and suggests the pulse-addition method is more reliable for measuring f . The value of f so obtained agreed with published values for sandy to loamy soils similar to the experimental soil at similar moisture contents (Rowell *et al.*, 1967; Moldrup *et al.*, 2001; Hamamoto *et al.*, 2009) and with values for such soils estimated with a theoretical model (Moldrup *et al.*, 2001).

Aldaba *et al.* (2010b) compared the pulse-addition method with the half-cell method for diffusion of radio-strontium, ^{85}Sr , in soil. They found a good correlation between D values obtained by the two methods, but the values with the pulse-addition method were consistently smaller for reasons which were not clear. They pointed out the pulse-addition

method had the advantage of requiring much smaller quantities of radioisotope to be handled.

The two methods share some common limitations. Both require careful preparation of the diffusion cells to ensure uniform bulk density and moisture content. Achieving uniform bulk density and moisture content is particularly challenging in soils with swelling clays (Staunton & Rees, 1988; Nimmo, 2004; Ng & Menzies, 2007). This was observed in the sandy loam soil used here when sieved to $< 212 \mu\text{m}$, but not in soil sieved to $< 500 \mu\text{m}$. Uniform soil moisture equilibration was achieved by wetting the soil to saturation and then draining on pressure plates.

While the pulse-addition method is preferred for studying the diffusion of non-adsorbed solutes, i.e. with constant D , the half-cell method is useful for the diffusion of sorbed solutes with concentration- or time-dependent diffusion coefficients (Bagshaw *et al.*, 1972; Pinner & Nye, 1982; Staunton & Nye, 1983), as is expected for U.

5.2 Measurements of U solid-solution partitioning

Measurements of U sorption in shaken suspensions of the experimental soil at different pHs and CO_2 pressures are presented in Chapter 3.

5.2.1 Effect of pH and CO_2 pressure

The results showed the commonly-observed (Catalano & Brown, 2005; Payne *et al.*, 2011; Kumar *et al.*, 2014; Uyuşur *et al.*, 2014) bell-shaped relation between sorption and pH, with a sorption maximum at around neutral pH, and the sorption maximum shifted to progressively lower pH as the CO_2 pressure increased. This is due to the dependence of both U speciation in solution and soil surface charge on both pH and CO_2 pressure (Li & Kaplan, 2012; Kerisit & Liu, 2014).

At $\text{pH} < 6.0$ the dominant species are UO_2^{2+} and UO_2CO_3 , whereas at higher pH $\text{Ca}_2\text{UO}_2(\text{CO}_3)_3$ and $\text{CaUO}_2(\text{CO}_3)_3^{2-}$ are dominant. Because UO_2CO_3 and $\text{Ca}_2\text{UO}_2(\text{CO}_3)_3$ are uncharged, they are largely not adsorbed on the soil solid. Whereas the UO_2^{2+} cation and $\text{CaUO}_2(\text{CO}_3)_3^{2-}$ anion are sorbed to an extent depending on pH-dependent positive and negative charges on soil surfaces (Liu *et al.*, 2013). Hence U sorption can change

abruptly in response to minor pH changes. Root-induced pH changes in the rhizosphere are often as much as 1 pH unit (Tinker & Nye, 2000), and so could strongly affect U sorption and hence diffusion to roots. It is therefore important to allow for such effects in models of U transport to and uptake by roots.

The trend of increasing U solubility with increasing pH was further enhanced by increase in CO₂ pressure due to increased concentrations of U-complexing carbonate ligands. The effect was less pronounced at pH 7.6 than at pH 7.0 due to saturation effect of available U in solution. This shows that the CO₂ pressure range applied covered well unsaturated soil conditions; CO₂ pressure above 5 kPa can be expected to make no significant difference to U solubility at similar U concentrations.

5.2.2 Effect of U concentration

The shaken suspension results were well-described with a Freundlich-type equation at each pH and CO₂ pressure, which was used to calculate the U buffer power, dC/dC_L , at different total U concentrations. Others have also used the Freundlich equation to describe U sorption (Hull, 2002; Dong *et al.*, 2006). The shaken suspension and modelling results indicate the U buffer power was more sensitive to pH and CO₂ pressure than to U concentration over the relevant range of concentrations. Nonetheless, the concentration-dependence was sufficient to conclude that assuming a constant value – i.e. a constant K_D – could lead to significant errors in diffusion calculations. This was also concluded by Tokunaga *et al.* (2004b) who compared measured D values with those calculated with a constant K_D and found that the latter overestimated sorption and retardation by an order of magnitude.

5.2.3 Sorption kinetics

It is commonly found that the initial adsorption or desorption of U in soil is followed by continuing slow sorption which may last for many weeks (Braithwaite *et al.*, 1997; Qafoku *et al.*, 2005; Handley-Sidhu *et al.*, 2009; Eagling *et al.*, 2013; Stoliker *et al.*, 2013). In general, the rate-limiting step in such slow sorption in soil is access to or from sorption sites within soil aggregates by diffusion in the intra-aggregate pore space, rather than slow chemical reactions on soil surfaces as such (Nye & Staunton, 1994;

Ptashnyk *et al.*, 2010; Shang *et al.*, 2011; Stoliker *et al.*, 2013). A limitation of shaken suspension experiments is that intra-aggregate diffusion is likely to be accelerated by convection and disaggregation of the soil. Hence measurements of sorption kinetics in shaken suspensions may over-estimate rates of sorption compared with the true kinetics in diffusion systems in which the soil solution is stationary. Hence, except at pH 6 where the C_L values were close to detection limits, the U buffer powers measured in shaken suspension in Chapter 3 were somewhat larger than those inferred from the diffusion profiles measured in Chapter 4 (as observed also by Tokunaga *et al.*, 2004), although they had similar sensitivities to pH and CO₂ pressure.

5.3 Model of U diffusion and reaction

A key objective of this thesis was to provide experimental evidence and parameters with which to test a mechanistic model of U transport in soil, appropriate for the time and distance scales of U uptake by plant roots. The earlier model of U uptake developed by Boghi *et al.* (2018) solves equations for U transport through soil to cylindrical plants roots and the simultaneous transport and effects of acids and bases through the soil in response to root-induced changes in soil pH and CO₂ pressure. The theory of the movement of acids and bases through soil is well established (Tinker & Nye, 2000). So the key element of Boghi *et al.*'s model to be tested was the treatment of U diffusion and reaction. Accordingly, in the experiments in Chapter 4, I measured concentration-distance profiles of U through soil at different constant pHs and CO₂ pressures, and in planar geometry to simplify the measurements. Two modelling approaches were compared: (a) an analytical solution of the appropriate diffusion equation for the experimental system with a constant diffusion coefficient (i.e. not allowing for concentration- or time-dependency), and (b) a numerical model based on that of Boghi *et al.* (2018). The model parameter values were derived from the measurements made in Chapters 2 and 3.

The results showed both models correctly predicted the broad effects of pH and CO₂ pressure on U diffusion. But the simple model with constant D failed to predict the observed concentration-distance profiles, mostly underestimating the diffusive flux of U through soil and not predicting the observed discontinuity at the boundary between the

source and the sink cells. In contrast, the numerical model predicted the profiles well, and could account for the discontinuity at the boundary by differences in the kinetics of U desorption in the source cell and adsorption in the sink cell.

This finding shows that it is important to consider not only fast but also slow sorption on the time- and length- scales relevant to plant uptake. The importance of slow local-equilibration processes suggests that soil structure and micro-aggregation and the distribution and abundance of reactive sites are key determinants of U sorption kinetics in real soils on the distance- and time- scale relevant to root uptake. This explanation agrees with Stoliker *et al.* (2013) and Shang *et al.* (2011) who found pore network structure, as indicated by particle size distribution and aggregation, greatly affected U surface complexation reactions. These conclusions point to the need to measure U sorption with the soil solution stationary, as in the half-cell diffusion system used here. Sorption measurements made in shaken suspensions or flow-through systems are likely to be misleading.

5.4 Further model development

The excellent agreement between the observed profiles and those obtained with the numerical model using input parameters that were measured or otherwise estimated independent of the concentration-distance profiles, shows that the model is a correct description of the system and all important processes are allowed for. Mechanistic models that have been tested and proven in this way can be used to make predictions for other parameter regimes and applications. This is a great advantage over empirical models whose predictions are limited to the experimental systems and parameter regimes they have been calibrated for (Nye, 1992; Sparks, 1999). The numerical model can be further applied to model U uptake by plants and processes in the rhizosphere affecting U mobility.

The model provides explicit evidence for the importance of the kinetics of U sorption, in addition to the effects of soil pH and CO₂ pressure, which were greater than the effects of U concentration. The model as tested does not allow for gradients in pH and CO₂ pressure through the soil, as are expected in the rhizosphere (Blossfeld *et al.*, 2013; Gérard *et al.*, 2017). Nor does it allow specifically for the effects of individual U-

complexing organic ligands, such as malate and citrate, which are known to significantly change U solubility and speciation in the rhizosphere (Tandy *et al.*, 2013). However, it would be a simple matter to incorporate such effects in the model without altering its basic framework.

5.5 Conclusions

5.5.1 Experimental methodology

- Most published data on U sorption kinetics have been obtained in shaken suspensions or from breakthrough curves in flow-through systems, where the rate-limiting processes are artificially altered by convection and disaggregation of the soil. Here I avoided these problems with the novel approach of inferring reaction kinetics from concentration-distance profiles of U in soil under rhizosphere-relevant conditions, so that the soil solution was stationary.
- The half-cell methods used had the additional advantage of providing information on both desorption, in the source cell, and adsorption, in the sink cell. The measured U concentration-distance profiles showed a distinct discontinuity at the source-sink interface, which was due to differences in the kinetics of desorption and adsorption.
- The strong dependence of U sorption on pH and CO₂ pressure found in the shaken suspension and diffusion experiments was in agreement with published data, and shows the importance of allowing for root-induced changes in pH and CO₂ pressure in the rhizosphere in models of U uptake by plants.
- The concentration-dependence of U sorption was less important than the effects of pH and CO₂ pressure. However, the observed concentration-dependence was sufficient to question the use of constant K_D values.

5.5.2 Modelling

- The simple model based on an analytical solution of the diffusion equation with a constant diffusion coefficient, ignoring concentration- and time-dependency of sorption, could not reproduce the observed concentration-distance profiles. This highlights the limitations of the shaken suspension approach used to measure U sorption parameters for the model.

- The numerical model based on that of Boghi *et al.* (2018) successfully predicted the measured U concentration-distance profiles, indicating the model correctly accounts for all important mechanisms.
- The sensitivity analysis of the model indicates that the important effects to be allowed for in modelling U uptake by roots are the effects of pH, CO₂ pressure and organic and inorganic ligands on U speciation and sorption, and the effects of sorption kinetics.

5.5.3 Future work

The following further work is suggested to develop a model suitable for investigating the mechanisms of U uptake by plants in contaminated soil.

1. *Mesocosm experiments.* The root-uptake version of the model should be tested in mesocosm experiments with soil planted with relevant plant species, with rates of U uptake measured over suitable periods. This should be accompanied by simultaneous monitoring of root-induced changes in pH, CO₂ pressure and other variables in the rhizosphere. The initial and final soil chemistry at the root-soil interface and in bulk soil should be well-characterised. Using the same experimental soil as here would facilitate this. Root-induced changes in rhizosphere pH could be manipulated by comparing plants fed with NH₄-N versus NO₃-N.
2. *Half-cell measurements.* To further test the model and its sensitivity to soil parameters, measurements of U diffusion and reaction should be made in a wide range of soils using the half-cell method developed here. Further U complexing ligands could be added to the soils reflecting root-induced changes in soil chemistry: (a) with the pH in the source cells differing from the sink cell according to differences measured in the above mesocosm experiments, and (b) one of the cells containing dominant root exudates identified.
3. *Verification of U speciation.* Sorption processes in this study are inferred from a “weight of evidence” rather than direct observation. This could be improved by employing spectroscopic methods to map the pore-scale distribution of sorbed U and its association with specific mineral and organic phases in the soil. This would

help further elucidate the mechanisms of U transport and reaction, and could help to further generalise sorption modelling.

4. *Field experiments.* Up-scaling of the single root model to whole-plant and field scales are necessary further steps to link this research to real soil systems. Further processes will intervene at such scales and need to be accounted for. For example, at the field scale, the non-uniform distribution of U within the soil profile and the effects of the field water regime will be important. The laboratory and modelling findings should be therefore corroborated against field measurement using a variation of U soil amendments with depth and with sampling strategy on single root uptake-, seasonal- and annual-timescale over a minimum two-year period. The collection site of the experimental soil at Henfaes Research Centre should be the selected location for the field trials. The mesocosm experiments should therefore use the same soil and living plant species. Davies *et al.* (2018) suggests using a community of several species, including mycorrhizae inoculation. Therefore, a simplified plant community adopted from the sampling site at Henfaes Research Centre would be preferable. As in the mesocosm experiments, the field experiments should be accompanied by monitoring of pH and CO₂ concentration in the soil. High spatio-temporal resolution optodes would provide visual information on their propagation without disturbing the system. The initial and final soil chemistry at the root-soil interface and in bulk soil should be well-characterised, possibly following the method of Tandy *et al.* (2013) using ‘Single-Cell- Sampling-and-Analysis’ and capillary electrophoresis.

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APPENDICES

Appendix A

A-1 Test of homogeneous soil packing and volumetric moisture content throughout the soil column

The achieved uniformity of soil bulk density and moisture content was very good ($sd = 0.01$) per soil core but also between replicates. The uniformity of moisture content was tested by slicing equilibrated soil columns (in triplicate) which were previously moisture-equilibrated on pressure plates (55 kPa; 10 days) and stored in a fridge for one month at 4°C. The soil moisture homogeneity is necessary to prevent mass flow of solute.

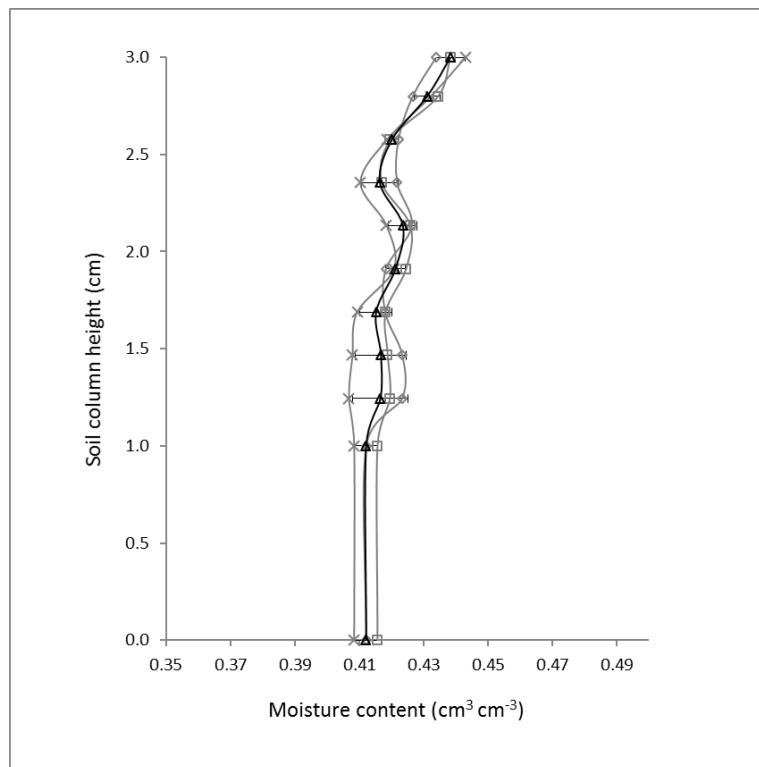


Figure A-1.1 Moisture-distance profile of soil columns packed with soil sieved to 500 micron and washed three-times with 0.01 M CaCl_2 , saturated with 0.01 M CaCl_2 , and drained at 0.55 bar suction to ≈ 0.41 moisture content (10 d). Grey solid lines are individual replicates; the black solid line is mean of the three replicates. Error bars are standard deviations of the mean profile.

A-2 Rejected replicates in pulse-addition method

The measured concentration-distance profiles of Br⁻ through the were plotted according to Equation (2-4). A number of replicate runs were prepared and the results are shown below. One of the replicates was lost during sectioning of the soil column due to adhesion of soil to the knife blade and others were rejected either for lack of linearity and/or insufficient number of datapoints above Br background. Material losses were avoided in later half-cell experiments by freezing the soil in liquid nitrogen before sectioning the column. Two replicates were evaluated as the most representative and are shown in the results section in Figure 2-6.

Table A-2.1 Rejected replicates for pulse-addition method. The range of ρ was 1.29-1.46 g cm⁻³ and θ was 0.36-0.46. The iterative method for background determination failed for some replicates denoted with *. The impedance factor, f , ranged from 0.05-0.94. The unrealistically low or high values correspond the failed background confirming robustness of the method and experimental problems. The linearity was assessed from r^2 and all replicates with $r^2 < 0.90$ were rejected.

Replicate	ρ g cm ⁻³	θ cm ³ cm ⁻³	Background Br μmol cm ⁻³	f	r^2
a	1.34	0.40	*	0.05	0.70
b	1.29	0.36	1.47E-02	0.07	0.98
c	1.32	0.39	*	0.07	0.97
d	1.31	0.40	*	0.08	0.80
e	1.46	0.38	7.10E-02	0.21	0.91
f	1.44	0.46	1.69E-01	0.37	0.90
g	1.42	0.36	*	0.63	0.89
h	1.42	0.36	*	0.94	0.94

*Br background concentration could not be calculated

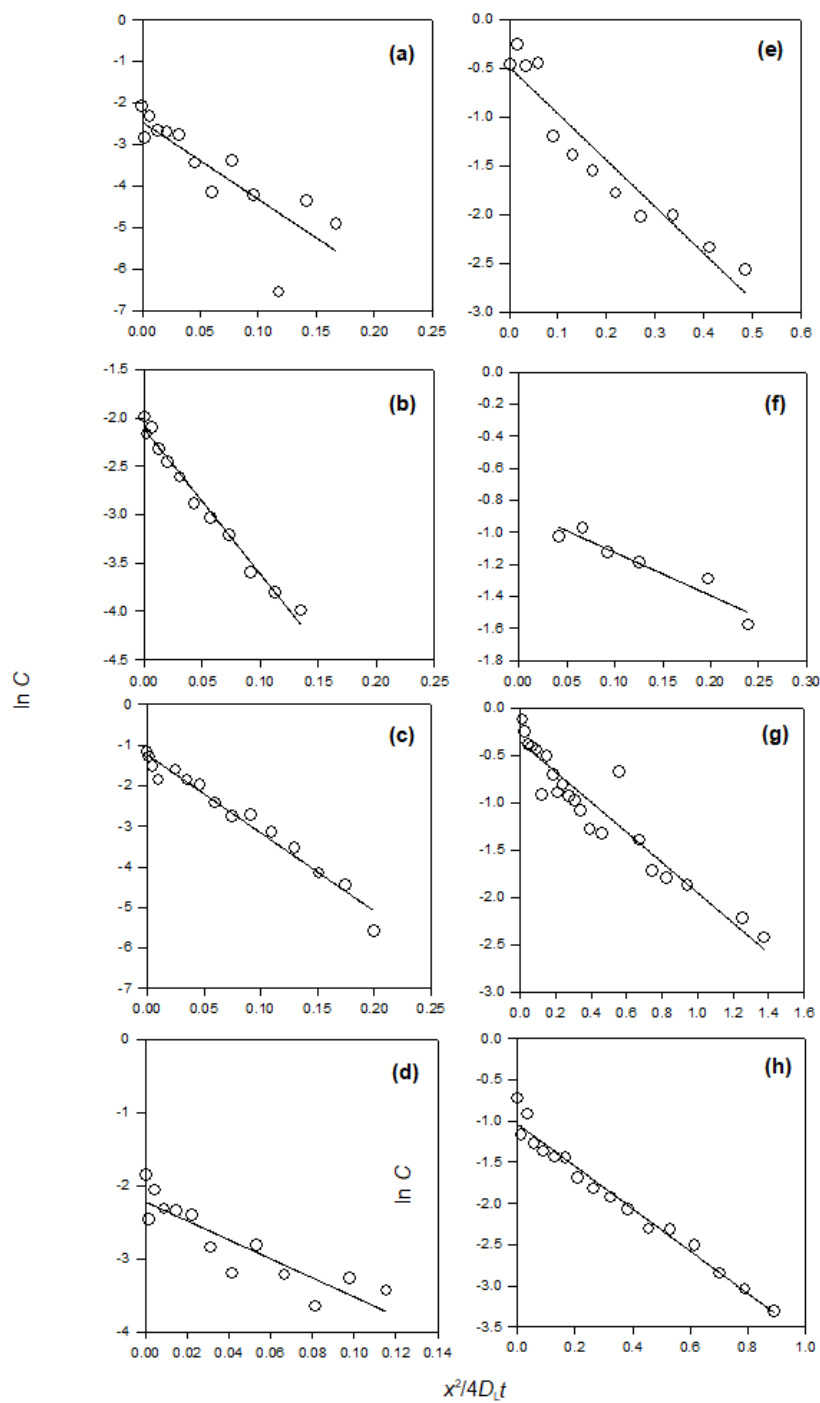


Figure A-2.1 Concentration-distance profiles of Br^- from 2-1 (C , $\mu\text{mol cm}^{-3}$ soil basis) following a pulse addition on one end of a soil column, plotted according to Equation (2-6). Data are measured concentrations; lines are fits to Equation (2-6). The ρ and θ of each replicated is given in Table A-2.1 together with calculated Br background and f , and r^2 of the linear fit.

Appendix B

B-1 Determination of U sorption equilibration time

The adsorption equilibrium was estimated from plots of time against adsorption percentage at time t , A_t :

$$A_t = \frac{m_s^{ads}(t_i)}{m_0} \times 100 (\%)$$

where A_t is the adsorption percentage at the time point t_i (%), m_s^{ads} is the mass of the solute adsorbed on the soil at adsorption equilibrium (μg), m_0 is the initial mass of the solute in the test tube (μg).

Uranium solutions at three concentrations (0.21 , 0.63 and $4.20 \times 10^{-3} \text{ mol L}^{-1}$) were tested over 240 h (12 collection times) at pH 6 and ambient CO_2 pressure. The pH was monitored in additional tube for any significant changes. The time at which the sorption reaches equilibrium was found to be almost instantaneous. To ensure sufficient time of equilibration in further experiments, 24 h shaking period was chosen, which is also the most commonly used shaking time in literature .

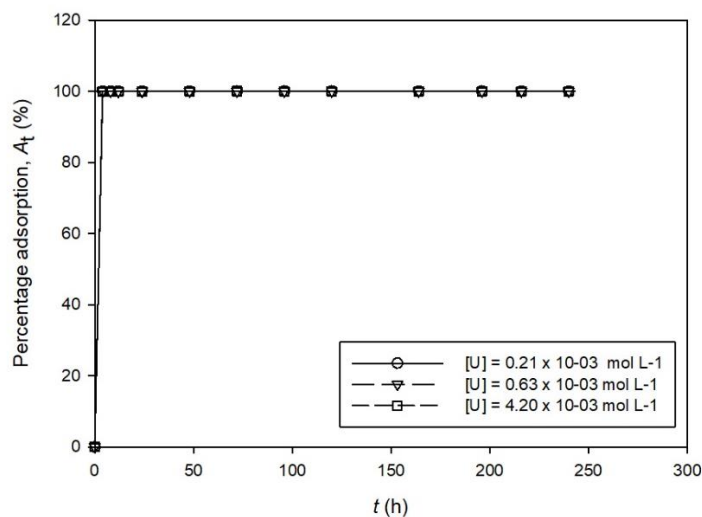


Figure B-1 Uranium sorption equilibration time determination at pH 6 and $p\text{CO}_2 = 1.26 \text{ kPa}$ for $[\text{U}] = 0.21, 0.63$ and $4.20 \times 10^{-3} \text{ mol L}^{-1}$. Error bars are almost invisible and represent mean standard deviation of three replicate samples.

B-2 Further results

Table B-2.1 The pH stability test in shaken suspensions under experimental conditions over 216 h period. The pH change was found negligible for all conditions

pH in shaken suspensions over 216 h						
Time (h)	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
0	6.03	7.0	7.6	6.15	6.85	7.57
2	5.89	6.98	7.59	6.10	7.08	7.52
5	5.99	7.05	7.65	6.15	6.93	7.63
8	5.90	7.08	7.66	6.00	7.00	7.63
12	6.00	-	7.64	6.10	7.22	7.62
24	6.28	7.03	7.61	6.21	7.05	7.41
48	6.09	7.15	7.66	6.10	6.93	-
72	6.23	6.92	7.56	6.10	7.00	7.49
96	6.11	7.09	7.54	6.14	6.95	7.58
168	6.05	7.17	7.64	6.02	6.90	7.50
216	-	7.11	7.63	6.21	7.13	7.57

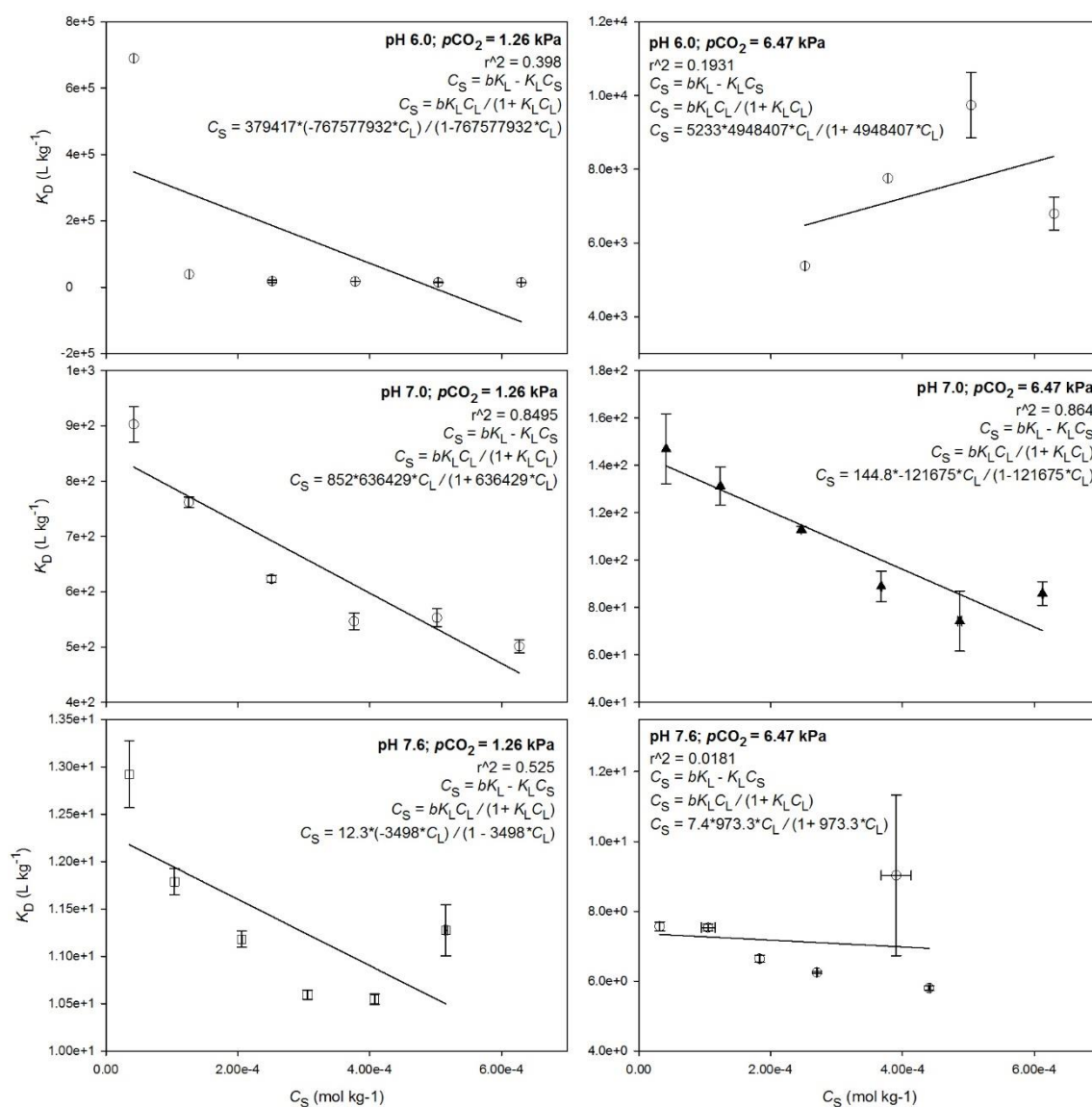


Figure B-2.2 Linearised fit of Langmuir isotherm. Applicability of the isotherm was tested by plotting distribution coefficient, K_D , against U concentration sorbed onto the solid, C_S . All fits where $r^2 < 0.95$ were rejected. Circles are observed data; lines are linear regressions. Experimental conditions are stated in individual plots.

B-3 Statistical analysis

B-3.1 One sample t-test for sorption kinetics experimental data

One sample t-test was performed for U sorption measurements over the 216 h period under each experimental condition (pH 6.0, 7.0 and 7.6; ambient or 5 kPa CO₂ pressure).

Results of the t-test showed significant differences within each group per condition. Therefore the results suggest sorption kinetic reactions over within the time of the experiments.

Statistical details

Population: N = 10

Degrees of freedom: 9

Significance difference: NO if $p > 0.05$; YES if $p \leq 0.05$

Table B-3.1 One sample t-test for the U sorption kinetics experiments

One sample t-test					
Condition	Mean	Std Dev	SEM	p	Significant difference
pH 6.0 & ambient $p\text{CO}_2$	11089.5	2472.3	781.8	$p \leq 0.001$	YES
pH 7.0 & ambient $p\text{CO}_2$	918.9	857.8	271.3	$p = 0.008$	YES
pH 7.6 & ambient $p\text{CO}_2$	13.6	4.7	1.5	$p \leq 0.001$	YES
pH 6.0 & $p\text{CO}_2 = 5$ kPa	7928.6	3263	1031.8	$p \leq 0.001$	YES
pH 7.0 & $p\text{CO}_2 = 5$ kPa	119.3	32.2	10.2	$p \leq 0.001$	YES
pH 7.6 & $p\text{CO}_2 = 5$ kPa	7.3	1.2	0.4	$p \leq 0.001$	YES

B-3.2 One way ANOVA for sorption kinetics experimental data

The groups represent K_D versus time, t (h), under the experimental range of pH and $p\text{CO}_2$ conditions. Labelling of each condition is explained in ‘Nomenclature’ section below. $[U] = 6.30 \times 10^{-1} \text{ mol L}^{-1}$. Other components were: $[\text{Ca}^{2+}] = 0.01 \text{ M}$, $[\text{Cl}^-] = 0.02 \text{ M}$.

The ANOVA results show that the median K_D values of the groups differed only between pH 6.0 and pH 7.0 under ambient CO_2 pressure, and between pH 6.0 at ambient CO_2 pressure and pH 7.6 (at both CO_2 pressures). However, some group comparisons were inconclusive (‘No test’).

One Way Analysis of variance for Sorption kinetics experiments

NOMENCLATURE

Label	Condition
A	pH 6.0 & ambient $p\text{CO}_2$
B	pH 7.0 & ambient $p\text{CO}_2$
C	pH 7.6 & ambient $p\text{CO}_2$
D	pH 6.0 & $p\text{CO}_2 = 5 \text{ kPa}$
E	pH 7.0 & $p\text{CO}_2 = 5 \text{ kPa}$
F	pH 7.6 & $p\text{CO}_2 = 5 \text{ kPa}$

(a) *Kruskal-Wallis test*

Where the differences in the median values among the groups were greater than would be expected by chance ($p \leq 0.001$), the differences were found statistically significant.

Kruskal-Wallis test			
Group	Median	25%	50%
A	11341.8	9957.6	12974.9
B	474.2	338.0	1513.5
C	11.2	10.3	17.5
D	7602.4	5363.9	9724.2
E	110.8	101.2	148.8
F	6.9	6.5	8.7

The results of the test with 5 degrees of freedom found statistically significant differences between the groups ($p \leq 0.001$).

(b) *Tukey test*

Multiple comparison of the mean group K_D values was done between all groups by Tukey test to isolate the group that differs from the others.

Group	Differences of ranks	p < 0.05
A vs F	478	Yes
A vs C	380	Yes
A vs E	279	Yes
A vs B	179	No
A vs D	58	No test
D vs F	420	Yes
D vs C	322	Yes
D vs E	221	No
D vs B	121	No test
B vs F	229	Yes
B vs C	201	No
B vs E	100	No test
E vs F	199	No
E vs C	101	No test
C vs F	98	No test
N = no significant difference between the rank sums		
Y = significant difference between the rank sums		
No test = no significant difference between the rank sums though one may appear to exist		

Appendix C

A. Supporting Information

Table S1 Maximum U influx into roots due to mass flow calculated with the data of Duquène *et al.* (2010) for uptake by ryegrass in a range of soils spiked with 36 mg U kg⁻¹. Seedlings were planted in the soils and root and shoot dry wt (m_{root} , m_{shoot}) and U concentrations (C_{root} , C_{shoot}) measured after 5 wk. U concentrations in the initial soil solutions (C_L) were also measured.

Soil	C_L (ug L ⁻¹)	m_{root} (g pot ⁻¹)	C_{root} (ug g ⁻¹)	m_{shoot} (g pot ⁻¹)	C_{shoot} (ug g ⁻¹)	U^a (mol pot ⁻¹)	Influx ^b (mol dm ⁻² s ⁻¹)	C_L (mol L ⁻¹)	Influx by mass flow ^c (mol dm ⁻² s ⁻¹)
A	13.3	0.29	34.5	1.16	0.12	4.26×10^{-8}	4.86×10^{-14}	5.59×10^{-8}	5.59×10^{-15}
B	3.9	0.23	7.8	1.30	0.03	7.70×10^{-9}	1.11×10^{-14}	1.64×10^{-8}	1.64×10^{-15}
C	3.3	0.39	10.6	1.85	0.02	1.75×10^{-8}	1.49×10^{-14}	1.39×10^{-8}	1.39×10^{-15}
D	37.2	0.35	39.8	1.45	0.14	5.94×10^{-8}	5.61×10^{-14}	1.56×10^{-7}	1.56×10^{-14}
E	10.3	0.35	27.9	1.58	0.05	4.14×10^{-8}	3.91×10^{-14}	4.33×10^{-8}	4.33×10^{-15}
F	7.7	0.26	67.8	1.61	0.24	7.57×10^{-8}	9.63×10^{-14}	3.24×10^{-8}	3.24×10^{-15}
G	5.5	0.35	21.5	1.41	0.04	3.19×10^{-8}	3.01×10^{-14}	2.31×10^{-8}	2.31×10^{-15}
H	6.5	0.40	25.5	1.45	0.09	4.34×10^{-8}	3.59×10^{-14}	2.73×10^{-8}	2.73×10^{-15}
I	95.7	0.16	270.5	0.88	2.36	1.91×10^{-7}	3.94×10^{-13}	4.02×10^{-7}	4.02×10^{-14}
J	18.7	0.34	21.1	1.27	0.11	3.07×10^{-8}	2.99×10^{-14}	7.86×10^{-8}	7.86×10^{-15}
K	33.3	0.22	41.9	1.41	0.38	4.10×10^{-8}	6.16×10^{-14}	1.40×10^{-7}	1.40×10^{-14}
L	16.3	0.27	10.6	1.37	0.03	1.22×10^{-8}	1.49×10^{-14}	6.85×10^{-8}	6.85×10^{-15}
M	4.1	0.25	6.5	1.33	0.02	6.94×10^{-9}	9.18×10^{-15}	1.72×10^{-8}	1.72×10^{-15}
N	27.8	0.56	20.6	1.89	0.04	4.88×10^{-8}	2.88×10^{-14}	1.17×10^{-7}	1.17×10^{-14}
O	23.1	0.32	23	1.34	0.12	3.16×10^{-8}	3.27×10^{-14}	9.71×10^{-8}	9.71×10^{-15}
P	23.4	0.49	23.8	1.46	0.08	4.95×10^{-8}	3.34×10^{-14}	9.83×10^{-8}	9.83×10^{-15}
Q	7.1	0.26	8.5	1.43	0.04	9.53×10^{-9}	1.21×10^{-14}	2.98×10^{-8}	2.98×10^{-15}
R	40.0	0.24	23.5	1.40	0.05	2.40×10^{-8}	3.31×10^{-14}	1.68×10^{-7}	1.68×10^{-14}

^a $U = \text{uptake} = (m_{\text{root}}C_{\text{root}} + m_{\text{shoot}}C_{\text{shoot}}) \times 10^{-6} / 238$.

^bInflux = $dU/dt / A$ where $A = \text{root surface area} = m_{\text{root}} \times \rho \times (\pi a^2 l / 2\pi a l) = m_{\text{root}} \times \rho \times a / 2$ where $\rho = \text{root density}$, $a = \text{root radius}$ and $l = \text{root length}$. We assume unit root density and $a = 0.002 \text{ dm}$ which is typical for grasses (Tinker & Nye 2000). We also assume $dU/dt = U/t$, which will be a several-fold underestimate because U will have been increasing near exponentially at $t = 5 \text{ wk}$.

^cInflux by mass flow = vC_L where $v = \text{water flux into the roots}$. We use $v = 10^{-7} \text{ dm s}^{-1}$ which is typical (Tinker & Nye 2000).

B. Further methods

CO₂ pressure in the soil air. Triplicate half-cells of soil prepared as for the concentration-distance profile measurements were 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% CO₂ in air through the box at 0.05 L min⁻¹. After 48 h, the cells were sliced axially into five sections and dissolved CO₂ in the soil solution measured as follows. Approx. 5 g subsamples of each section were placed in centrifuge filtration units (Millipore Ultrafree Centrifugal Filter Device with a 0.22 µm membrane), capped and then centrifuged at 4,000 *g* for 15 min, collecting the soil solution. Dissolved CO₂ concentrations in the soil solutions were measured within a few minutes of collection using a micro-electrode (MI-720 electrode, Microelectrodes Inc, USA). Calibration solutions (0.25–10 % CO₂) were prepared by dissolving NaHCO₃ in CO₂-free ultra-pure water. The values were $P_{\text{CO}_2} = 1.3 \pm 0.1$ and 6.5 ± 0.1 kPa in the ambient and elevated treatments, respectively, approximately constant along the length of the cells.

Analysis of U in soil digests. 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, with rf forward power 1540 W and reflected power 1 W, and Ar gas flows of 0.81 L min⁻¹ and 0.19 L min⁻¹ for carrier and makeup flows, respectively. Solutions were aspirated by a micro-mist nebuliser at a rate of 1.2 mL min⁻¹. The instrument was operated in spectrum acquisition mode. Three replicate samples were analysed per sample. Standards were prepared from a single element stock solution (1000 µg U L⁻¹, PlasmaCal, SPE Science) 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) diluted 100-fold to give 100 µg U L⁻¹.

C. Further results

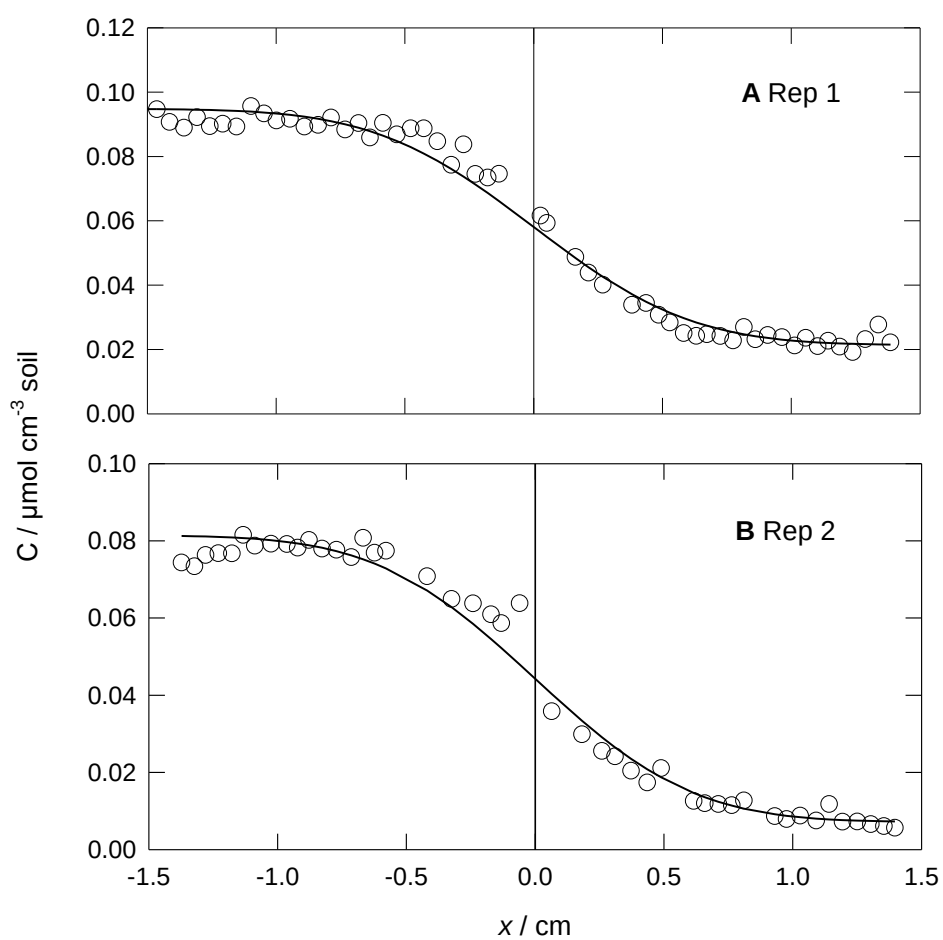


Figure S1. Measured (points) and calculated (lines) concentration-distance profiles of Br measured by the half-cell method for two replicates.

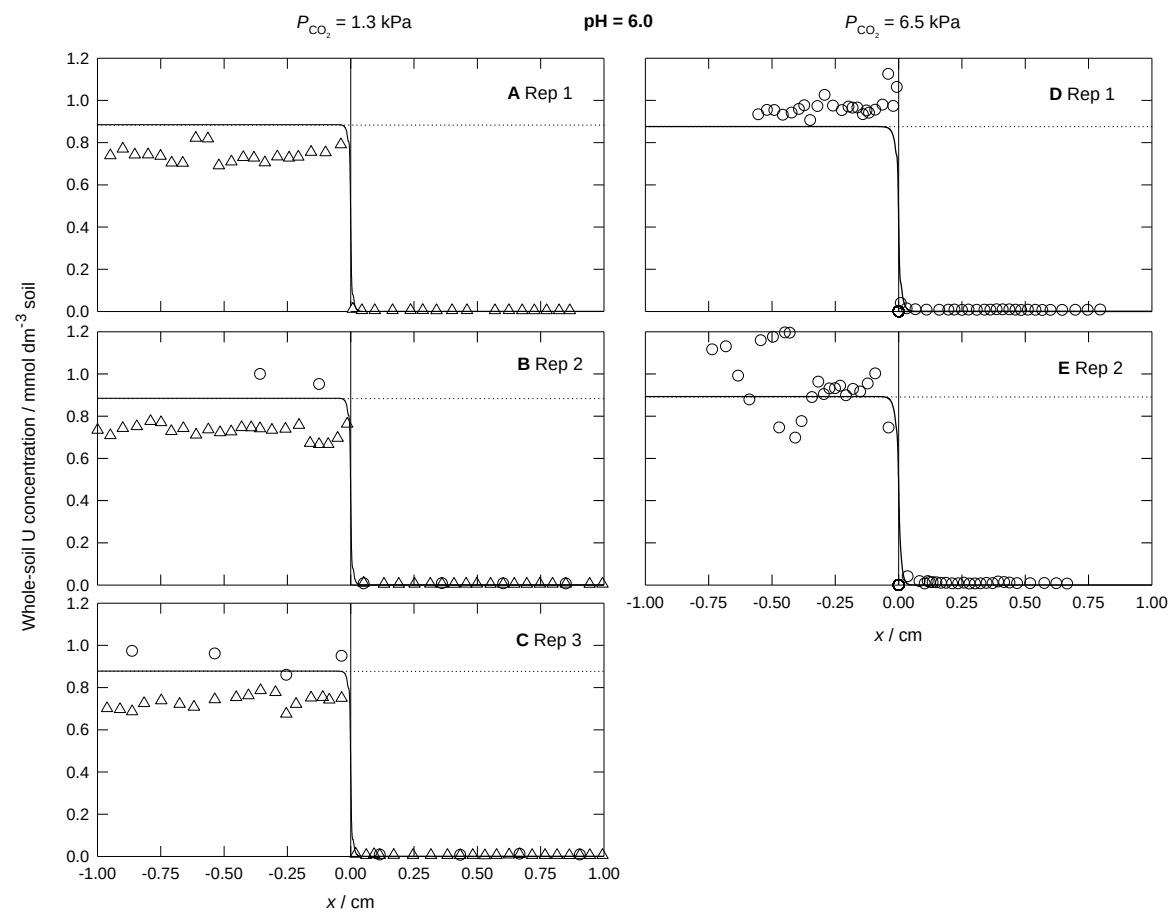


Figure S2. Measured and calculated concentration-distance profiles of U for all replicates at pH 6.0. Rep 3 at $P_{\text{CO}_2} = 6.5$ kPa failed.

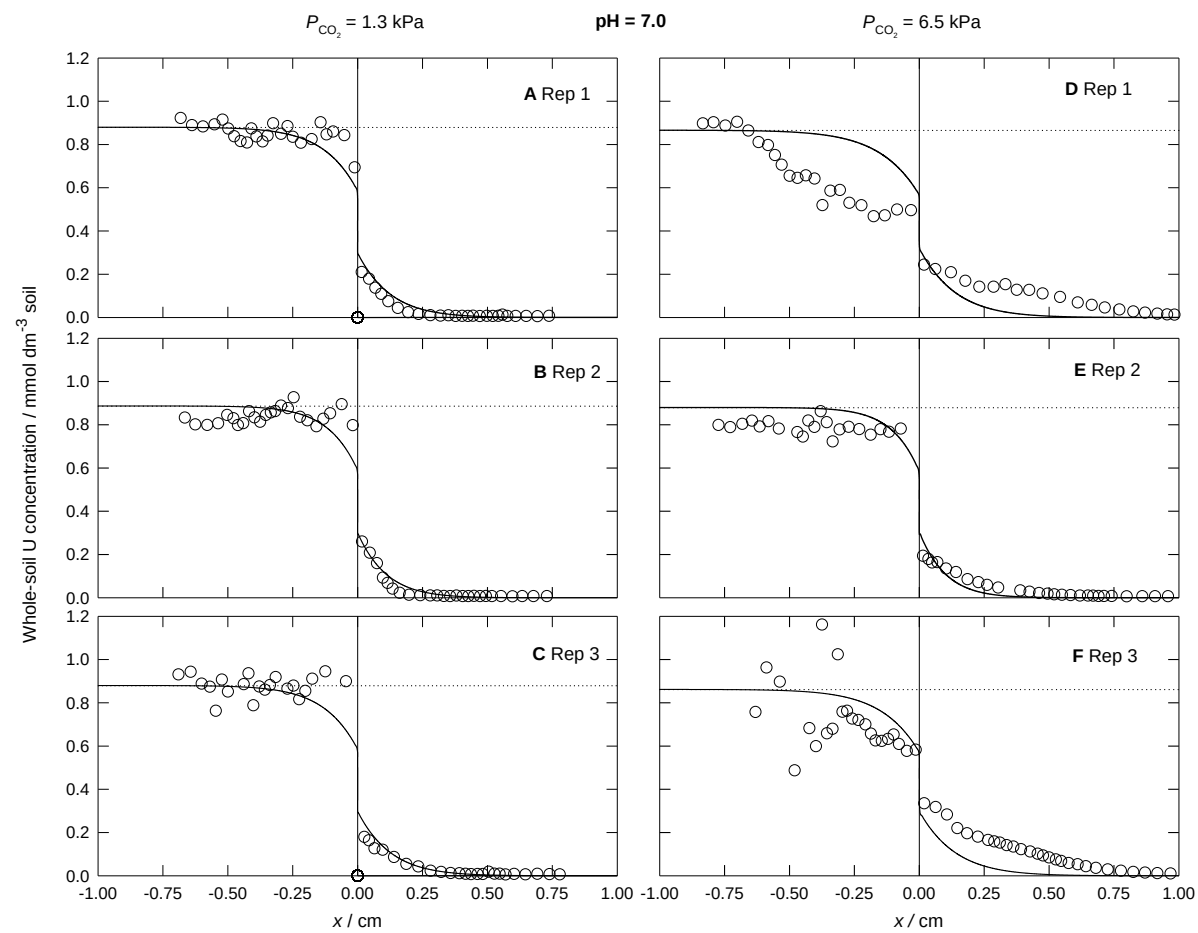


Figure S3. Measured and calculated concentration-distance profiles of U for all replicates at pH 7.0.

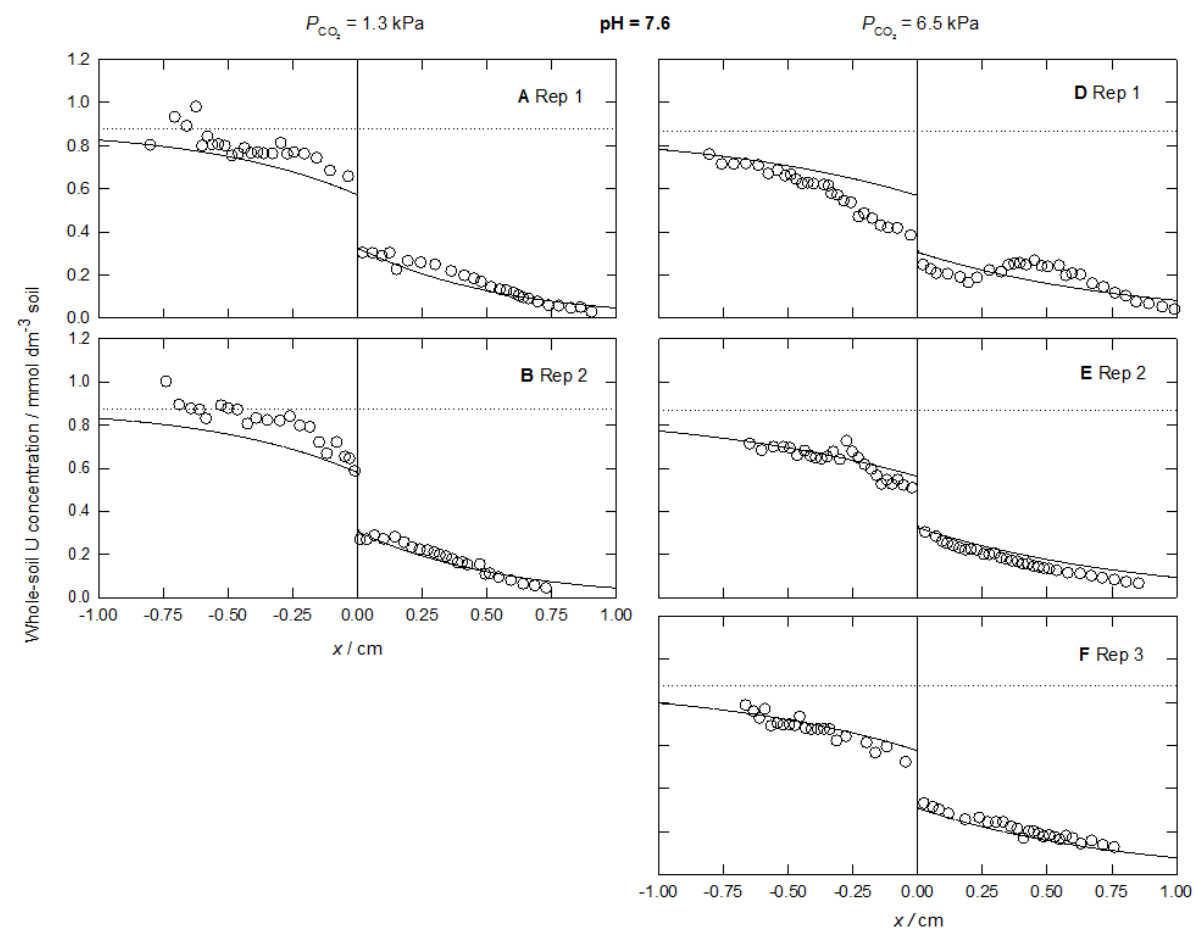


Figure S4. Measured and calculated concentration-distance profiles of U for all replicates at pH 7.6. Rep 3 at $P_{\text{CO}_2} = 1.3$ kPa failed.

