A STUDY OF URANIUM SPECIATION IN SURFACE FRESHWATERS USING DIFFUSIVE GRADIENTS IN THIN FILMS

by

Jiujiang Zhao

MS (Chinese Academy of Science, China)

A thesis submitted to the Faculty of Graduate Studies and Research
in partial fulfillment of the requirements for the degree of
Doctor of Philosophy

Department of Chemistry
Carleton University
Ottawa, Ontario
Canada

April 2009

Copyright © 2009

Jiujiang Zhao

Library and
Archives Canada

Published Heritage
Branch

395 Wellington Street
Ottawa ON K1A 0N4
Canada

Bibliothèque et
Archives Canada

Direction du
Patrimoine de l'édition

395, rue Wellington
Ottawa ON K1A 0N4
Canada

Your file Votre référence
ISBN: 978-0-494-52078-9
Our file Notre référence
ISBN: 978-0-494-52078-9

NOTICE:

The author has granted a non-exclusive license allowing Library and Archives Canada to reproduce, publish, archive, preserve, conserve, communicate to the public by telecommunication or on the Internet, loan, distribute and sell theses worldwide, for commercial or non-commercial purposes, in microform, paper, electronic and/or any other formats.

The author retains copyright ownership and moral rights in this thesis. Neither the thesis nor substantial extracts from it may be printed or otherwise reproduced without the author's permission.

AVIS:

L'auteur a accordé une licence non exclusive permettant à la Bibliothèque et Archives Canada de reproduire, publier, archiver, sauvegarder, conserver, transmettre au public par télécommunication ou par l'Internet, prêter, distribuer et vendre des thèses partout dans le monde, à des fins commerciales ou autres, sur support microforme, papier, électronique et/ou autres formats.

L'auteur conserve la propriété du droit d'auteur et des droits moraux qui protègent cette thèse. Ni la thèse ni des extraits substantiels de celle-ci ne doivent être imprimés ou autrement reproduits sans son autorisation.

In compliance with the Canadian Privacy Act some supporting forms may have been removed from this thesis.

Conformément à la loi canadienne sur la protection de la vie privée, quelques formulaires secondaires ont été enlevés de cette thèse.

While these forms may be included in the document page count, their removal does not represent any loss of content from the thesis.

Bien que ces formulaires aient inclus dans la pagination, il n'y aura aucun contenu manquant.

Canada

Abstract

The objective of this research was to study uranium speciation using Diffusive Gradients in Thin Films (DGT) in freshwaters. Diffusion in the diffusive layer and metal binding by the binding layer were studied in model solutions and in freshwater samples. The effective uranium concentration was defined and used along with the DGT lability factor to interpret the experimental results. The percentage distribution of uranium species and the apparent lability factor, which reflected both mobility and lability of uranium species, were obtained using data fitting.

These studies revealed that the distribution of uranium species varied with the speciation parameters in surface freshwaters. A strong complexing agent, such as humic acid, reduced the percentage of DGT-labile uranium species, whereas competition between trace metals (e.g. copper) and uranium for binding with humic substances increased the percentage of DGT-labile uranium species. The percentage of uranium DGT-labile species increased with increasing ionic strength in model solutions, indicating that ionic strength might affect the binding of uranium with humic substances. At higher pH, the percentage of DGT-labile uranium species increased because of the formation of inorganic uranium species, such as $\text{UO}_2(\text{OH})_3^-$. With increasing NaHCO_3 concentration, the percentage distribution of $\text{UO}_2(\text{CO}_3)_2^{2-}$ had the same trend as the percentage of DGT-labile uranium species, indicating it had a higher apparent lability factor. There was some impact of atmospheric CO_2 on the uranium uptake by DGT in U-HA ($\text{HA} < 0.6 \text{ mg L}^{-1}$) and U-FA ($\text{FA} < 1 \text{ mg L}^{-1}$) model solutions.

The uranium binding kinetics was investigated using Competitive Ligand Exchange Method (CLEM) to obtain quantitative data on the lability of uranium complexes in aqueous media. It was found that with increasing HA concentrations, the labile fraction of uranium species decreased. The labile component in natural surface water samples was most probably uranium-carbonate species, whereas the non-labile component was the uranium bound to the strong binding sites of dissolved organic carbon (DOC). The lability factor for DGT experiment, α , can be obtained using CLEM.

To improve the DGT performance, an electric potential was applied on the traditional DGT device. The new DGT device has an enhanced analytical sensitivity, and it is suitable for alkaline waters.

To demonstrate the practical utility of DGT in routine operations, field studies were performed in the Rideau Cannel, Ottawa, Ontario, Canada. The relationship between the DGT labile species and the speciation parameters was obtained by correlation analysis. A significant positive correlation between the Chelex-100 DGT labile species and the concentration of calcium was found, indicating that calcium might increase the DGT-labile fractions of uranium.

Acknowledgements

I am very grateful to my supervisor, Professor C.L. Chakrabarti (a.k.a. Chak) for his continued support, guidance and encouragement. I should like to thank my thesis co-supervisor, Professor Jack Cornett who gave me direction and invaluable support to my Ph.D. Thesis research.

I am grateful to Professor John Murimboh of Acadia University, NS, for research consultation. I should also like to thank all the other members of Chak's research group: Dr. Ismail Al-Fasrous; Dr. Jeff Guthrie; Cathy Murimboh; Dr. Nouri Hassan; Dr. Tahir Yapici; Dr. Rong Wang; Dr. Parthasarathi Chakraborty; Min Yang; Jianfu Deng; Sheren Boca and Yamini Gopalapillai. Because of their association, my stay at Carleton University has been a pleasant and fruitful experience.

I should also like to thank Dr. Conrad Grégoire, Dr. Chunsheng Li, Dr. Weijia Li and Dr. Dominic Lariviere, and my research collaborators at Carleton University, at Radiation Protection Bureau, Health Canada and at Geological Survey of Canada. They gave me valuable support to my research work.

I am grateful to Radiation Protection Bureau, Health Canada for supporting my Ph.D. study financially during its five-year Ph.D. program.

My grateful acknowledgements are due to NSERC Discovery Grants research funds for materials, supplies and equipment used in this research project.

Finally, I should like to thank my parents for their unconditional love and support.

Table of Contents

Abstract	ii
Acknowledgements	iv
Table of Contents	v
List of Tables	ix
List of Figures	xii

Chapter 1 Introduction	1
1.1 Introduction	2
1.2 Statement of the problem and our response	2
1.3 Current state of knowledge	3
1.3.1 Metal speciation and bioavailability in Natural Waters	3
1.3.2 Humic substances	8
1.3.3 Uranium speciation and bioavailability in surface freshwaters	10
1.3.4 Impact of atmospheric carbon dioxide on uranium speciation	11
1.4 Weakness of current speciation techniques	13
1.5 Hypothesis and Objective	14
1.6 Theoretical Background	16
1.6.1 Transport process	16
1.6.2 Principle of DGT	16
1.6.3 Computational Speciation Models	17
1.7 Outline of the thesis	18
1.7.1 Characterizations of diffusion and binding layers	18
1.7.2 Study of uranium DGT-labile species in aquatic systems	19
1.7.3 Development of an advanced method using DGT	19
1.7.4 Field studies	20
1.8 References	21
Chapter 2 Diffusive gradients in thin-films (DGT)	25
2.1 Theory	26
2.1.1 Principle of DGT	26
2.1.2 Diffusive layer	29
2.1.3 DGT binding layer	30
2.1.4 DGT-labile species	31
2.1.5 Applications of DGT	32
2.2 Experimental	34
2.2.1 Reagents	34
2.2.2 Preparation of gel for DGT	34
2.2.3 Assembly and deployment of DGT	36
2.2.4 Determination of uranium concentration	36
2.2.5 QA/QC	37
2.3 References	40

Chapter 3 Diffusion coefficients of uranium species	42
3.1 Introduction.....	43
3.1.1 Thermodynamic view of diffusion	43
3.1.2 Diffusion coefficient and mobility.....	44
3.1.3 Diffusion coefficient and temperature	45
3.1.4 Statistical view of diffusion	46
3.1.5 Types of diffusion modes	47
3.2 Experimental.....	48
3.2.1 Reagents.....	48
3.2.2 Preparation of diffusive gel	49
3.2.3 Determination of diffusion coefficient	49
3.3 Results and discussion	51
3.3.1 Diffusion coefficient of uranium	51
3.3.2 Donnan potential and ionic strength	51
3.3.3 The effect of pH on the overall diffusion coefficient of uranium.....	52
3.3.4 Overall diffusion coefficients of uranium in the carbonate and the bicarbonate model solutions	56
3.3.5 Diffusion coefficient of uranium in humic acid model solutions	60
3.3.6 Uranium species concentration on the surface of DGT binding layers	64
3.4 References.....	67
Chapter 4 Characterization of DGT binding layers.....	69
4.1 Introduction.....	70
4.2 Experimental.....	73
4.2.1 Reagents.....	73
4.2.2 Preparation of polymer-A DGT binding layers	74
4.2.3 Determination of uranium uptake by DGT binding layers	75
4.3 Results and discussion	76
4.3.1 Effect of immersion time on uranium uptake by DGT binding layers	76
4.3.2 Effect of pH on uranium uptake by DGT binding layers	81
4.3.3 The effect of ionic strength on uranium uptake by DGT binding layers...	86
4.3.4 Swelling effect	91
4.3.5 DGT deployment in synthetic fresh water samples	91
4.3.6 Field studies in natural surface freshwaters.....	94
4.4 Conclusions.....	96
4.5 References.....	98
Chapter 5 DGT-labile uranium species in aquatic systems	100
5.1 Introduction.....	101
5.1.1 DGT-labile species	101
5.1.2 Effective uranium concentration.....	103
5.1.3 Humic substance as metal-binders.....	106
5.2 Experimental.....	107
5.2.1 Reagents.....	107
5.2.2 The preparation of DGT diffusive layers and binding layers	108
5.2.3 Model solutions	108

5.2.4	DGT deployment	108
5.2.5	Determination of uranium.....	109
5.3	Results and discussion	109
5.3.1	Overall diffusion coefficient D_U and overall lability factor α_U in reference model solution	109
5.3.2	Effective uranium concentration in humic acid and fulvic acid model solutions.....	110
5.3.3	Competition of copper and uranium in model solutions	116
5.3.4	Ionic strength effect	117
5.3.5	The pH effect on uranium DGT-labile species in U-HA model solutions	118
5.3.6	Effect of carbonate ion on uranium DGT-labile species in U-HA model solutions.....	121
5.4	Conclusions.....	127
5.5	References.....	128
Chapter 6 Kinetic studies of uranium speciation—the lability factor α.....		130
6.1	Introduction.....	131
6.1.1	Competitive Ligand Exchange Method	131
6.2	Experimental.....	134
6.2.1	Reagents.....	134
6.2.2	Model Solutions and Synthetic fresh Water Samples.....	135
6.2.3	Natural Water Samples	136
6.2.4	Ligand exchange experiment.....	136
6.3	Results and discussion	137
6.3.1	Effect of the U(VI)/HA ratio on kinetic parameters	138
6.3.2	Effect of pH on kinetic parameters.....	144
6.3.3	Kinetic Parameters in the Natural Waters and the Synthetic fresh Water Sample	145
6.3.4	Adjunctive and Disjunctive Pathways	152
6.4	Conclusions.....	156
6.5	References.....	157
Chapter 7 Development of DGT device by applying electric potential		159
7.1	Introduction.....	160
7.1.1	Limitations of the current DGT technology	160
7.1.2	Theory	160
7.2	Experimental.....	163
7.2.1	Instrument	163
7.2.2	Preparation of polyacrylamide gel and Chelex-100 resin gel.....	163
7.2.3	Assembly of the New DGT device	163
7.2.4	Experimental procedure.....	166
7.3	Results and discussion	167
7.3.1	Uranium in gel electrode solution.....	167
7.3.2	Electric field parameter, κ , in the uranium-sodium bicarbonate model solutions.....	167

7.3.3	Recovery of uranium from the new DGT device at various uranium concentrations levels.....	169
7.3.4	Experimental time and uranium uptake by the new DGT device.....	170
7.3.5	Uranium uptake by the new DGT device in the uranium-sodium acetate buffer, at pH 4.5.....	172
7.3.6	Uranium uptake by the new DGT devices at high applied potential and at high ionic strength	172
7.3.7	Field applications.....	175
7.4	Conclusions.....	179
7.5	References.....	180
Chapter 8	Field studies.....	181
8.1	Introduction.....	182
8.2	Experimental.....	182
8.2.1	Deployment site	182
8.2.2	Experimental procedures	182
8.2.3	QA/QC.....	183
8.3	Results and discussion	186
8.3.1	Speciation parameters.....	186
8.3.2	Uranium uptake by DGT binding layers	194
8.3.3	Correlation analysis	201
8.4	References.....	206
Chapter 9	Conclusions	207
Appendix A	- Impact of atmospheric CO₂ on the uranium speciation	212
Appendix B	- Stability constants of uranium species	235

List of Tables

Table 1.1	Analytical methods for determining uranium speciation	15
Table 2.1	Instrument operating conditions for Elan 6100 DRC ICP-MS	36
Table 2.1	Concentrations of uranium in Certified Reference Materials and their certified values. (Determined using ICP-MS)	39
Table 3.1	Overall diffusion coefficient of uranium D_U and percentage distribution of uranium species in the source solutions at different pHs.	54
Table 3.2	The percentage distribution of uranium species in the source solutions at pH 8, calculated using the computer program Visual Minteq.	55
Table 4.1	Major inorganic ions, total organic (TOC) and inorganic (TIC) carbons in synthetic fresh water samples.	92
Table 4.2	Major inorganic ions, total organic(TOC) and inorganic carbons (TIC) in St. Lawrence River in the summer of 2006	95
Table 4.3	Overall assessment of DGT binding layers	97
Table 5.1	Percentage distribution of uranium species in the HA model solutions. Uranium concentration $100 \mu\text{g L}^{-1}$, HA concentration: $0.1\text{-}20 \text{ mg L}^{-1}$, Cu $50, 100 \mu\text{g L}^{-1}$, pH 7. θ_{Uw} represents the percentage of uranium binding with weak binding sites, whereas θ_{Us} represents the percentage of uranium binding with strong binding sites.	115

Table 5.2	Percentage distribution of uranium species (%) in uranium-HA model solutions, calculated using Visual MINTEQ program. Uranium concentration was 100 $\mu\text{g L}^{-1}$, HA concentration 2 mg L^{-1} , NaNO_3 0.001 mol L^{-1} , pH: 5, 6, 7, 8, 9, and 10. ϕ represents the apparent lability factor of the uranium species in those model solutions.	122
Table 5.3	Percentage distribution of uranium species (%) in uranium-HA model solutions, calculated using Visual MINTEQ program. Uranium concentration was 100 $\mu\text{g L}^{-1}$, HA concentration 2 mg L^{-1} , NaNO_3 0.01 mol L^{-1} , NaHCO_3 0.1, 0.5, 1, 2, 5 and 10 mmol L^{-1} . ϕ represents the apparent lability factor of uranium species in these model solutions.	126
Table 6.1	Kinetically distinguishable components in U(VI)-HA model solutions, ammonium acetate concentration 0.01 mol L^{-1} , uranium concentration 20 $\mu\text{g L}^{-1}$	141
Table 6.2	Kinetically distinguishable components in U(VI)-HA model solutions without the ammonium acetate buffer, pH 7.0; uranium in 0.01 mol L^{-1} ammonium acetate buffer, pH 7.0; and uranium in 0.004 mol L^{-1} sodium bicarbonate, pH 10. Uranium concentration 20 $\mu\text{g L}^{-1}$	143
Table 6.3	Major inorganic ions, total organic and inorganic carbon in St. Lawrence River and in synthetic lake water samples	149
Table 6.4	Kinetically distinguishable components of uranium species in St. Lawrence River water and in synthetic lake water samples. Uranium concentration was 10 $\mu\text{g L}^{-1}$	150
Table 8.1	Recovery of natural water CRMs	184

Table 8.2	Trace metal concentrations in the Rideau Canal water samples during the DGT deployment period.	191-192
Table 8.3	Concentration of calcium and magnesium in the Rideau Canal water samples during the DGT deployment period.	193
Table 8.4	Uranium uptake by DGT in the Rideau Canal water samples during the DGT deployment period.	196
Table 8.5	Percentage of DGT-labile uranium species (%L) calculated by various DGT binding layers in the Rideau Canal water	203
Table 8.6	Correlation coefficients of percentage of DGT-labile uranium species (%L) and speciation parameters in Rideau Canal (total uranium concentration, temperature, pH, electrical conductivity, TOC, IC, calcium and magnesium concentrations.)	205

List of Figures

Figure 1.1	Metal-organism interactions	5
Figure 1.2	Schematic of biotic ligand model for the acute toxicity of metals.	7
Figure 1.3	A proposed structure of humic acid	10
Figure 2.1	DGT device assembly	26
Figure 2.2	A schematic diagram of the principle of DGT	27
Figure 2.3	Diagram of poly(4-styrenesulfonate) (PSS) liquid binding phase DGT device	31
Figure 2.4	Metal-ligand complex (ML) in DGT experiment	32
Figure 2.5	Comparison of uranium concentrations in DGT samples determined using KPA and ICP-MS.	38
Figure 3.1	Diagrams of the diffusion modes	48
Figure 3.2	Diagram of diffusion cell	50
Figure 3.3	Overall diffusion coefficients of uranium in different pHs.	53
Figure 3.4	Uranium concentration in the receiver solution as a function of experimental time. Source solution: uranium concentration 1 mg L ⁻¹ , Na ₂ CO ₃ 1000 mg L ⁻¹ .	57
Figure 3.5	Uranium concentration in the receiver solution as a function of experimental time. Source solution: uranium concentration 1 mg L ⁻¹ , NaHCO ₃ 1000 mg L ⁻¹ .	58

Figure 3.6	Inorganic carbon concentration in the receiver solution as a function of experimental time. Source solution: uranium concentration 1 mg L ⁻¹ , Na ₂ CO ₃ 1000 mg L ⁻¹ .	59
Figure 3.7	Inorganic carbon concentration in the receiver solution as a function of experimental time. Source solution: uranium concentration 1 mg L ⁻¹ , NaHCO ₃ 1000 mg L ⁻¹ .	60
Figure 3.8	Uranium concentration in receiver solution as function of experimental time. Source solution: uranium concentration 2 mg L ⁻¹ , HA 10 mg L ⁻¹ , pH 7.	62
Figure 3.9	Organic carbon concentration in receiver solution as function of experimental time. Source solution: uranium concentration 2 mg L ⁻¹ , HA 10 mg L ⁻¹ , pH 7.	63
Figure 3.10	Organic carbon concentration in receiver solution as function of experimental time. Source solution: uranium concentration 2 mg L ⁻¹ , HA 20 mg L ⁻¹ , pH 7.	64
Figure 3.11	Linear diffusion gradient in diffusive gel layers in model solutions.	66
Figure 4.1	Change of the binding groups of Chelex-100 resins with increasing pH.	71
Figure 4.2	Function groups of DE-81	72
Figure 4.3	Function groups of cellulose phosphate	72
Figure 4.4	Function groups of polymer-A, (salicylaldoxime-3,5-diyl (N,N'-dimethylethylenediamine N,N'-bismethylene))	73

Figure 4.5	The effect of immersion time on uranium uptake by Chelex-100 DGT binding layer in uranium model solutions, pH 7. Initial concentration of uranium: 1.0 mg L^{-1} .	78
Figure 4.6	The effect of immersion time on uranium uptake by DE 81 and Chelex-100 DGT binding layers at pH 8.0, 23°C with initial uranium concentration of 1.0 mg L^{-1} and NaHCO_3 concentration of 100 mg L^{-1} .	79
Figure 4.7	The effect of immersion time on uranium uptake by P81 binding layers in 1 mg L^{-1} uranium model solutions, pH 7.	80
Figure 4.8	The effect of immersion time on uranium uptake by polymer-A DGT binding layer in 1 mg L^{-1} uranium model solutions, pH 7.	81
Figure 4.9	Effect of pH on uranium uptake by Chelex-100 DGT binding layer in $100 \mu\text{g L}^{-1}$ uranium model solutions.	83
Figure 4.10	Effect of pH on the uranium uptake of DE 81 and Chelex-100 DGT binding layers. Initial uranium concentration: 1.0 mg L^{-1} .	84
Figure 4.11	Effect of pH on uranium uptake by P81 DGT binding layer in $100 \mu\text{g L}^{-1}$ uranium model solutions.	85
Figure 4.12	Effect of pH on uranium uptake by polymer-A DGT binding layer in $100 \mu\text{g L}^{-1}$ uranium model solutions.	86
Figure 4.13	Effect of ionic strength on uranium uptake by Chelex-100 DGT binding layer in $100 \mu\text{g L}^{-1}$ uranium model solutions.	87
Figure 4.14	Effect of ionic strength on uranium uptake by DE 81 and Chelex-100 DGT binding layers.	88

Figure 4.15	Effect of ionic strength on uranium uptake by P81 binding layers in $100 \mu\text{g L}^{-1}$ uranium model solutions, pH 7.	89
Figure 4.16	Effect of ionic strength on uranium uptake by polymer-A DGT binding layers in $100 \mu\text{g L}^{-1}$ uranium model solutions, pH 7.	90
Figure 4.17	DGT mass-time curves for synthetic fresh water. (DE81 and Chelex-100)	93
Figure 4.18	DGT mass-time curves for synthetic fresh water. (Polymer-A DGT and Chelex-100 DGT).	94
Figure 5.1	Percentage of DGT-labile uranium species (%) as a function of the HA concentration, in uranium-HA model solutions. Uranium concentration $100 \mu\text{g L}^{-1}$, HA concentration: 0.1, 0.5, 1, 2, 3, 4 and 5 mg L^{-1} .	113
Figure 5.2	Percentage of DGT-labile uranium species (%) as a function of the FA concentration, in uranium-FA model solutions. Uranium concentration $100 \mu\text{g L}^{-1}$, NaNO_3 0.01 mol L^{-1} , FA concentration: 0.1, 0.5, 1, 2, 5 and 10 mg L^{-1}	114
Figure 5.3	Percentage of DGT-labile uranium species (%) as a function of HA concentration, in uranium-HA model solutions. Uranium concentration $100 \mu\text{g L}^{-1}$, NaNO_3 0.01 mol L^{-1} , HA concentration: 0.1, 0.5, 1, 2, 5 and 10 mg L^{-1} .	119
Figure 5.4	Percentage of DGT-labile uranium species (%) as a function of pH, in uranium-HA model solutions. Uranium concentration $100 \mu\text{g L}^{-1}$, HA concentration 2 mg L^{-1} , NaNO_3 0.001 mol L^{-1} ,	120

Figure 5.5	Percentage of DGT-labile uranium species (%) as a function of concentration of NaHCO_3 , in uranium-HA model solutions. Uranium concentration $100 \mu\text{g L}^{-1}$, HA concentration 2 mg L^{-1} , NaNO_3 0.01 mol L^{-1} , concentration of NaHCO_3 0.1, 0.5, 1, 2, 5 and 10 mmol L^{-1} .	123
Figure 5.6	Percentage distributions of $\text{UO}_2(\text{CO}_3)_2^{2-}$ (%) as a function of concentration of NaHCO_3 , in uranium-HA model solutions. Uranium concentration $100 \mu\text{g L}^{-1}$, HA concentration 2 mg L^{-1} , NaNO_3 0.01 mol L^{-1} , concentration of NaHCO_3 0.1, 0.5, 1, 2, 5 and 10 mmol L^{-1} . Calculated using Visual MINTEQ program.	125
Figure 6.1	Diagram of CLEM experiment.	137
Figure 6.2	Ligand exchange kinetics for three U(VI)/HA ratios in model solutions at pH 6.0.	140
Figure 6.3	Ligand exchange kinetics for U(VI)/HA in model solutions with U(VI)/HA ratio 0.1 at different pH values.	147
Figure 6.4	Ligand exchange kinetics of uranium species in St. Laurence River and synthetic lake water samples.	148
Figure 6.5	Predicted uranium speciation (% total uranium) in synthetic lake water as function of pH (2 to 12) calculated using Visual MINTEQ.	151
Figure 6.6	Ligand exchange kinetics for U(VI)/HA with different Chelex-100 concentration in model solutions when U(VI)/HA ratio is 0.001.	155
Figure 7.1	New DGT device Assembly (step 1)	164
Figure 7.2	New DGT device Assembly (step 2)	165

Figure 7.3	New DGT device Assembly (step 3)	166
Figure 7.4	Uranium uptake by the new DGT devices as a function of applied potential, uranium- sodium bicarbonate model solutions. Uranium concentration $100 \mu\text{g L}^{-1}$, NaHCO_3 concentration 0.01 mol L^{-1} , pH 8.	169
Figure 7.5	Uranium uptake by the new DGT device in uranium- sodium bicarbonate model solutions. Uranium concentration 0.1, 1, 10 and $100 \mu\text{g L}^{-1}$, NaHCO_3 0.01 mol L^{-1} , pH 8.	170
Figure 7.6	Uranium uptake by the new DGT devices as a function of experimental time, in uranium- sodium bicarbonate model solutions. Uranium concentration $100 \mu\text{g L}^{-1}$, NaHCO_3 0.01 mol L^{-1} , pH 8. Applied potential +3 V.	171
Figure 7.7	Uranium uptake by the new DGT device as a function of the applied potential, uranium in acetic acid/acetate buffer (NaAc-HAc) model solutions. Uranium concentration $100 \mu\text{g L}^{-1}$, NaAc-HAc 0.01 mol L^{-1} , pH 4.5.	173
Figure 7.8	Uranium uptake by the new DGT device as a function of the applied potential, uranium- sodium bicarbonate model solutions. Uranium concentration $100 \mu\text{g L}^{-1}$, NaHCO_3 0.01 mol L^{-1} , pH 8. Experimental time 1 hour. Applied potential 0-200 V.	174
Figure 7.9	New DGT device Assembly for field work (step 1)	176
Figure 7.10	New DGT device Assembly for field work (step 2)	177
Figure 7.11	Calibration curve of New DGT device for field study in model solutions. Uranium $10\text{-}200 \mu\text{g L}^{-1}$ and sodium bicarbonate 0.01 mol L^{-1} . Applied potential +9V.	178

Figure 8.1	Map of DGT deployment site at Rideau Canal	185
Figure 8.2	Temperature in the Rideau Canal water measured during deployment period.	187
Figure 8.3	pH in the Rideau Canal water measured during deployment period.	188
Figure 8.4	Electrical conductivity in the Rideau Canal water measured during deployment period.	189
Figure 8.5	TOC and IC in the Rideau Canal water measured during deployment period.	190
Figure 8.6	Uranium concentration in the Rideau Canal water samples.	195
Figure 8.7	Effective uranium concentration in the Rideau Canal water measured by Chelex-100 DGT.	197
Figure 8.8	Effective uranium concentration in the Rideau Canal water measured by DE81 DGT.	198
Figure 8.9	Effective uranium concentration in the Rideau Canal water measured by P81 DGT.	199
Figure 8.10	Effective uranium concentration in the Rideau Canal water measured by Polymer-A DGT.	200
Figure 8.11	Percentage of DGT-labile uranium species (%L) during the deployment period.	204

Chapter 1

Introduction

1.1 Introduction

The speciation of uranium in natural waters is very complex, and progress is hindered by the lack of direct analytical techniques and methods for the quantitative determination of trace quantities of uranium species in unpolluted natural waters. This lack poses a great challenge to environmental research scientists. This work presents the results of investigation into the uranium speciation in natural surface freshwaters, using a novel technique: Diffusive Gradients in Thin Films (DGT). DGT offers an exciting promise of determination of uranium speciation present in natural surface freshwaters at trace levels.

1.2 Statement of the problem and our response

Uranium is one of the heavy metals in the natural environment, and it exists in a variety of physicochemical forms: uranyl ion, uranium-organic and inorganic complexes – each with its own unique properties. The impact assessment of uranium in the natural environment for a risk assessment is ultimately concerned with how the uranium species directly and indirectly affects biota (i.e., their bioavailability and toxicity). Traditional environmental regulatory measures for uranium are based on total uranium concentration. However, the toxicity of uranium is dependent not only on the total uranium concentration, but also, and more importantly, on the speciation of the uranium. Because of the pH-dependence of uranium speciation in natural waters, compounded by shifting chemical equilibria of carbonate and bicarbonate species, natural waters present a challenge to unraveling the mysteries of these competing equilibria. Our understanding of uranium speciation in natural surface freshwaters is limited by the enormous complexity of naturally-occurring complexants, such as humic substances, which are ubiquitous in

natural waters. The overall goal of this study is to provide a more comprehensive knowledge and understanding of uranium speciation in natural surface freshwaters, which is essential for the environmental impact assessment of uranium. An analytical technique that can meet the above challenge must have the required sensitivity and selectivity. The DGT technique offers the promise of such a technique, and has the added advantage of enhanced analytical sensitivity by virtue of its internal pre-concentration mechanism. Its greatest advantage is that by constraining the mass transport by means of a sufficiently thick diffusive layer, DGT has the capability of quantifying a so-called DGT-labile species—an operationally-defined species, characterized by the mobility and lability of metal species.

1.3 *Current state of knowledge*

1.3.1 Metal speciation and bioavailability in Natural Waters

The word “speciation” in analytical chemistry is borrowed from biological sciences to express the specific chemical forms of an element in a system. The term “chemical speciation” as used by environmental scientists has different meanings, depending on the purpose and the nature of determination. It is often used to denote detailed metal-species distribution in studies of synthetic (model) solutions, in which each metal species can be characterized[1].

The International Union for Pure and Applied Chemistry (IUPAC) has defined elemental speciation in chemistry as follows[2]: “

- (i) Chemical species. Chemical elements: specific form of an element defined as to isotopic composition, electronic or oxidation state, and/or complex or molecular structure.
- (ii) Speciation analysis. Analytical chemistry: analytical activities of identifying and/or measuring the quantities of one or more individual chemical species in a sample.
- (iii) Speciation of an element; speciation. Distribution of an element amongst defined chemical species in a system. ”

Since it is often not possible to determine the concentrations of all the species of an element, the term fractionation is used and is defined as follows.

- (iv) “Fractionation. Process of classification of an analyte or a group of analytes from a certain sample according to physical (e.g., size, solubility) or chemical (e.g., bonding, reactivity) properties. ”

The specific physicochemical form of a metal (e.g. free metal ion or metal ligand complex), which has been used as the determinant of transport, fate and bioavailability of the metal in natural waters, is of importance[3]. The distribution of metal species (i.e. metal speciation) is therefore important for predicting the impacts of metal species on the environment [4].

The interactions between trace metals and organisms are very complex and are still not adequately known (Figure 1.1). The interactions of trace metal species with aquatic organisms may involve the following steps [5, 6]:

- 1) The metal species transport from in the bulk solution to the cell membrane surface.
- 2) The metal species bind with the binding sites on the cell membrane surface
- 3) The metal species diffuse through the cell membrane into the organism (uptake by organism)

Several models have been used to predict the metal bioavailability and toxicity.

Figure 1.1 Metal-organism interactions[7]

The Free Ion Activity Model (FIAM), which has been proposed by Morel[8] as a predictor for metal bioavailability in the aquatic environment, is based on the assumption that the bioavailability of the metal and its toxicity to organisms is dependent on the free metal ion activity, rather than the total metal concentrations[6]. The goal of the FIAM is to predict the bioavailability and toxicity of a metal as a function of the free metal ion activity in aqueous media. One assumption of the FIAM is that the metal species are at equilibrium at the surface of the biological membrane. The requirement for the assumption to be true is that the formation and dissociation kinetics and transport of the metal species towards the biological membrane is rapid compared to the metal uptake by the organism, so that it is not the rate-determining step. Only under those conditions, is the assumption of chemical equilibrium valid. However, many exceptions to the FIAM have been reported [9-11]. In natural waters, the water chemistry is much more complex than in the model solutions used in laboratory-based experiments; therefore the assumption of chemical equilibrium is probably not fulfilled in the case of application of FIAM to natural water samples.

Brown et al. [10] has integrated the concepts of FIAM into Biological Receptor Theory (BRT) to obtain a more rigorous conceptual model, which more precisely quantifies the process of chemical species adsorption at biological receptor sites. Another extension of FIAM is the Fish Gill Surface Interaction Model[12], which predicts bioavailability of metals by incorporating measured metal-gill surface binding constants into a geochemical speciation model[13].

An equilibrium-based model, the Biotic Ligand Model (BLM) [14, 15], is a computer-based program designed to assess the acute ecological effects of metals to the organism in aquatic systems (Figure 1.2). The BLM framework shares the features with earlier metal bioavailability models, such as the Gill Surface Interaction Model and the Free Ion Activity Model. The formulation and the assumptions of the BLM are almost same as those of the FIAM, but the BLM considers also the impacts of competing cations and ligands[14].

Figure 1.2 Schematic of biotic ligand model for the acute toxicity of metals[15].

1.3.2 Humic substances

Humic substances (HS), which are natural organic matter (NOM), are major constituents of the organic matter in soils, sediments and natural waters. Metal speciation in natural waters is largely controlled by NOM [16-19]. Naturally-occurring complexants, such as humic and fulvic acids, as well as inorganic complexants, such as carbonate and bicarbonate are ubiquitous in freshwaters. Unlike simple inorganic ligands, humic substances are both chemically and physically heterogeneous. Hence, HS cannot be isolated from environmental samples in a pure state, but only as homologous compounds [19, 20].

The heterogeneity results from the following characteristic features of HS:

Polydispersity. Humic substances, which consist of fulvic acid, humic acid and humin, represent a variety of different molecules with a wide range of molecular sizes and masses [21, 22].

Polyfunctional properties. Each macromolecule of HS contains a large number and variety of functional groups with different intrinsic binding properties, including carboxylic, phenolic, salicylic and nitrogen-bearing functional groups (Figure 1.3). Metal binding sites in HS can be divided into two types: major binding sites and minor binding sites[19].

The major site types, which are large in number (90-99% of the total sites present), are carboxylate and phenolate functional groups; while minor sites comprise a small fraction of the total sites but a large number of the site types, including N- and S- bearing functional groups[23]. Although minor sites comprise only a small fraction of the total number of sites, they may be the most important sites for controlling the extent of metal complexation in aquatic systems [19, 24] .

Polyelectrolytic properties. The functional groups in HS undergo dissociation at appropriate pHs, forming anionic moieties with negative charges (polyanions). When metal cations react with one functional group of polyanions, the binding of metal ion can be greatly strengthened by the coulombic attraction from the neighbouring, non-reacting, negative functional groups. The total electric charge depends on the pH and degree of site occupation by the metals [17, 18, 25].

Conformational properties. pH, ionic strength, the electric charge and degree of hydration of the macromolecules may influence the conformational properties, and consequently affect the stability of metal-HS complexes. Conformational changes may also result in changes in the physicochemical properties of humic substances [26-28].

Figure 1.3 A proposed structure of humic acid[3]

1.3.3 Uranium speciation and bioavailability in surface freshwaters

Uranium has 16 known isotopes, all of which are radioactive. In nature, U consists of a mixture of three isotopes: ^{238}U (99.276%), ^{235}U (0.718%), and ^{234}U (0.0056%)[29]. As one of the heavy metals, uranium presents both radioactive and chemical toxicity. Various body systems (human and animal) are affected by uranium [30-33]. The toxicity of uranium to organisms in aquatic systems has been also reported[34]. The bioavailability of uranium in surface freshwaters is dependent on its chemical speciation, which is influenced by its physicochemical parameters in surface freshwaters, including pH, ionic strength, concentration of humic substances (HS) and other parameters[20].

Durrance[35] has reported the uranium content for uraniferous terrain as $1\text{--}10\ \mu\text{g L}^{-1}$ in surface water, $1\text{--}150\ \mu\text{g L}^{-1}$ in groundwater and $15\text{--}400\ \mu\text{g L}^{-1}$ in uranium mine water. Canada has some of the world's largest reserves of high-quality raw uranium, and this poses a potential problem for Canadian surface freshwaters if a relatively large quantity of raw uranium results in a discharge of uranium into natural waters. Environmental concentration ranges previously reported for uranium in Canadian surface waters were $0.10\text{--}2.1\ \mu\text{g L}^{-1}$ for the Pacific region; $0.097\text{--}2.14\ \mu\text{g L}^{-1}$ for the western region; $0.28\text{--}0.65\ \mu\text{g L}^{-1}$ for the central region, and; $0.25\text{--}0.73\ \mu\text{g L}^{-1}$ for the Atlantic region[36].

Uranium exists as various chemical species in natural waters, including uranyl ion, and complexes with inorganic and organic ligands (both anion and cation) [37]. Humic substances(fulvic acid[38], humic acid[39], and humin), which represent typically 40%-99% of Dissolved Organic Carbon(DOC)[40], are important complexing agents for uranium in natural waters at neutral or low pH.

1.3.4 Impact of atmospheric carbon dioxide on uranium speciation

Carbon dioxide (CO_2) is a trace gas, which is about 0.03% in earth's atmosphere[41]. Dissolved inorganic carbon species, H_2CO_3 , CO_2 (aq), HCO_3^- and CO_3^{2-} in natural waters can exchange with atmospheric CO_2 and carbonate in rocks (limestone rocks). Those reactions occur in three phases: air, water and rock[42].

Two idealized equilibrium systems need to be considered: closed system and open system. In a closed system, a limited quantity of CO_2 distributes between the gas and water phase.

Equilibrium concentrations correspond to the Henry's Law constants, however, the proportions in the gas and water phase depend on the ratio of the volumes of water and gas[43].

In an open system, the partial pressure of CO₂ is considered as constant. If we assume the atmospheric CO₂ is 0.03% in earth's atmosphere, the solubility of atmospheric CO₂ in pure water at 25°C can be calculated according to Henry's Law:

$$p_{CO_2} = K_{CO_2} \cdot x_{CO_2} \quad (1.1)$$

Where K_{CO_2} is Henry's Law constant, $K_{CO_2} = 1.25 \times 10^6$ mmHg (25°C)[44].

p_{CO_2} is the partial pressure of atmospheric CO₂, $p_{CO_2} = 0.03\% \text{ atm} = 0.228 \text{ mmHg}$ x_{CO_2} is the mole fraction of CO₂ dissolved in water,

$$x_{CO_2} = n(CO_2) / [n(CO_2) + n(H_2O)] \approx n(CO_2) / n(H_2O)$$

Assuming CO₂ is dissolved in 1 L pure water, $n(H_2O) = 1000/18 = 55.56 \text{ mol}$, the dissolved CO₂ in 1 L water is about $1.01 \times 10^{-5} \text{ mol}$ ($4.5 \times 10^{-4} \text{ g}$). Therefore the concentration of dissolved CO₂ in pure water equilibrated with atmospheric CO₂ at 25°C is about 0.45 mg L^{-1} ($0.12 \text{ mg L}^{-1} \text{ C}$).

In closed systems (model solutions), the partial pressure of CO₂ at equilibrium is less than that in open systems. The concentration of dissolved CO₂ in pure water in closed systems should be less than 0.45 mg L^{-1} .

However the natural water systems and the model solutions used in this thesis are not at equilibrium with the atmosphere at any given time. The kinetics of CO₂ absorption and

the equilibrium time depend on the flux of CO₂, J_{CO_2} and the depth of water column, h , which is the ratio of volume to surface area[45]:

$$\frac{dC_T}{dt} = J_{CO_2} \frac{Area}{Volume} = \frac{J_{CO_2}}{h} \quad (1.2)$$

where C_T is total dissolved carbon, t is time. Chemical reactions (e.g. acid-base reaction) can also affect the equilibrium of atmospheric CO₂ with water. The chemical equilibria in a U(VI)-H₂O-CO₂(g) system can be described as[46]:

where $(OH)_2CO_2^{2-}$ represents CO_3^{2-} , the pH in that system decreases during absorption of CO₂ and the forward reaction is favored with increasing pH.

To investigate the atmospheric CO₂ impact on the model solutions used in this thesis, the absorption rate of CO₂ in the model solutions has been studied and the impact on uranium speciation has been evaluated. Those results are presented in Appendix A.

1.4 Weakness of current speciation techniques

Many analytical methods are applied for uranium speciation, as presented in Table 1.1. These methods can be grouped into: 1) invasive techniques, which require pretreatment or separation, and 2) non-invasive techniques, which analyze samples directly[20]. Although several speciation techniques have been used to study uranium speciation, Time-Resolved Laser-Induced Fluorescence Spectroscopy (TRLIF) is the only analytical technique able to directly determine specific uranium species, but is limited in use to freshwaters of high pH and ionic strength[20]. Also, it suffers from another limitation: the quenching effect of carbonate, which reduces the fluorescence of uranium-carbonate

species [20, 47]. TRLIF is not suitable for *in-situ* measurement, which is the most important requirement for a monitoring program for uranium toxicity in aqueous systems. A recently invented technique, Diffusion Gradients in Thin Films (DGT), which was developed by Zhang and Davison [48, 49], promises to fill this serious knowledge gap. The process of DGT is similar to the metal uptake by micro-organisms or by plant roots[50]; therefore, DGT should be a suitable probe for metal species in surface waters, and may prove to be an effective probe of monitoring uranium speciation in surface waters.

1.5 Hypothesis and Objective

On the basis of the literature reports cited, more robust analytical techniques for determining the chemical speciation of uranium in natural surface freshwaters are needed before a link between the chemical speciation of uranium and its bioavailability can be established. The key hypothesis of this thesis is that the recently developed metal speciation technique, Diffusive Gradients in Thin Films (DGT), can be deployed *in-situ* for quantitative determination of uranium speciation in natural surface freshwaters with satisfactory analytical sensitivity and selectivity (freedom from interferences). Within the framework outlined above, the overall objective of this work is to test the above hypothesis.

Table 1.1 Analytical methods for determining uranium speciation[20]

Analytical Method	Analyte Uranium Species
Ultrafiltration	Dissolved and colloidal U in water
Dialysis	Dissolved and colloidal U in water
Gel filtration	UO_2^{2+} and uranyl-humic complexes in water
Size exclusion chromatography-ICP-MS	Dissolved and colloidal U (U complexation with humic and fulvic acids) in water
Ion exchange chromatography-ICP-MS	Oxidation state (U[IV] or U[VI]) in water
Capillary electrophoresis	Uranyl complexation with humic and fulvic acids in water
Cathodic stripping voltammetry	Labile uranyl species in water
Cathodic stripping chronopotentiometry	Labile uranyl species in water
Time-Resolved Laser-Induced Fluorescence Spectroscopy	UO_2^{2+} and individual uranyl hydroxide, phosphate carbonate, sulphate, arsenate and fulvic acid complexes in water
Chemical (sequential) extraction	Operationally defined U fractions in solids
X-ray absorption near-edge structure spectroscopy	Oxidation state (U[IV] or U[VI]) in solids and water
Electron energy loss spectroscopy	Oxidation state (U[IV] or U[VI]) in solids
Optical luminescence spectroscopy	Coordination (near-neighbour) structure of UO_2^{2+} in solids and water
X-ray absorption fine structure spectroscopy	Coordination (near-neighbour) structure of UO_2^{2+} in solids and water
X-ray photoelectron spectroscopy	Oxidation state (U[IV] or U[VI]) and coordination (near-neighbour) structure of UO_2^{2+} in solids
Photothermal (photoacoustic) spectroscopy	Coordination (near-neighbour) structure of UO_2^{2+} in solids

1.6 Theoretical Background

1.6.1 Transport process

If a single driving force X acts on one species, the corresponding flux, J , of this species is

$$J = LX \quad (1.4)$$

where L is a phenomenological coefficient, a scalar quantity corresponding to a generalized conductance or to the reciprocal of a generalized resistance[51].

Four basic transport processes can be differentiated as[51]:

1. Diffusion: transport of matter as a result of difference in the chemical potential (passive transport)
2. Heat conduction: transport of energy in temperature gradients.
3. Convection: transport of mass or energy results from the action of external forces.
4. Conduction of electric current: transport of electric charge and charged particles in an electric field.

DGT, which is based on the passive diffusion gradients, avoids the interference of the convection and is a controlled measurement that can be used as a speciation tool in surface freshwaters.

1.6.2 Principle of DGT

DGT is a speciation tool, consisting of a diffusion layer and a binding layer. When DGT is deployed in aqueous media, the metal species (free metal ions and metal complexes), which diffuse through the diffusion layer, either react with the binding layer directly

(Adjunctive Pathway), or react with the binding layer after dissociation (Disjunctive Pathway). The scientific background of DGT has been discussed in Chapter 2.

1.6.3 Computational Speciation Models

Many models, such as MINTEQA2, GEOCHEM, the Windermere Humic Aqueous Model (WHAM), and the Consistent Non-Ideal Competitive Adsorption (NICCA)-Donnan Model, have been used to model metal speciation in natural waters. In this work, the Visual MINTEQ program has been used to calculate the uranium speciation in model solutions and surface freshwaters. The stability constants of uranium species used in this thesis has been shown in Appendix B.

The Stockholm Humic Model (SHM), which can provide a more realistic assessment of metal-humic complexation than the Gaussian DOM model, has been used to interpret the uranium-humic substances interaction in Visual MINTEQ. A full description and discussion of the SHM for aqueous speciation is available in Gustafsson (2001)[52].

1.7 Outline of the thesis

This thesis has been divided into four parts:

1. Behaviors of uranium in diffusion and binding processes. (Characterizations of diffusive layer and binding layers)
2. Study of uranium DGT-labile species in aquatic systems (using DGT and Kinetic Models)
3. Development of an advanced method of DGT
4. Field studies

1.7.1 Characterizations of diffusion and binding layers

The diffusion coefficient is one of the important parameters of DGT. The diffusion properties of uranium and uranium complexes have been presented in **Chapter 3** of this thesis. The diffusion coefficients of CO_3^{2-} and HCO_3^- have also been presented in Chapter 3.

In **Chapter 4**, uranium binding by DGT binding layers has been discussed. Chelex-100 resin, ion-exchange filter membranes (DE-81 and P-81) and a new polymer binding layer: Poly (salicylaldoxime-3,5-diyl (N,N'-dimethylethylenediamine N,N'-bismethylene)) have been used as DGT binding layers. The results of performance of DGT binding layers at different pH, ionic strength have also been presented.

1.7.2 Study of uranium DGT-labile species in aquatic systems

In **Chapter 5**, the percentage of DGT-labile uranium species has been defined and then used to interpret the data obtained by DGT in uranium model solutions. The investigation also included study of the competition of copper with uranium for binding with HA and FA. The apparent lability factor and the percentage distribution of uranium species have been obtained by data fitting.

In **Chapter 6**, kinetic speciation of uranium in model solutions containing uranium and humic acid (HA), and in natural waters has been investigated using the Competitive Ligand Exchange Method (CLEM) to obtain information about the lability factor of uranium-HA complexes. The uranium speciation of every sample has been characterized either as “labile” or “non-labile” uranium complexes, depending on the dissociation rate coefficients of the complexes.

1.7.3 Development of an advanced method using DGT

To test the technique to improve the performance of DGT devices, an electric potential has been applied to the traditional DGT device. The advantages of electric potential are as follows:

1. With the above improved DGT device, the mass of metal accumulated in the DGT resin binding layer increases significantly.
2. The metal flux can be easily controlled by adjusting the voltage; the higher the voltage the faster the metal transport.

3. Metal species can be differentiated by the electric field, because of the different electric charges they carry. This is especially important for uranium, because uranium species in freshwaters have both negative and positive electric charges.

The effect of pH, ionic strength effect and other speciation parameters on the performance of the new DGT devices have been studied and these results have been presented in **Chapter 7**.

1.7.4 Field studies

DGT offers promise of an ideal technique for *in-situ* analysis. In this work, field studies have been undertaken using DGT as a probe in order to determine the uranium speciation in real natural surface freshwater systems. The field studies have been done at the several sampling sites. The results of the long-term field study have been presented in **Chapter 8**.

1.8 References

1. Cornelis, R. (2003). Handbook of elemental speciation : techniques and methodology. In Handbook of elemental speciation : techniques and methodology. (Chichester, West Sussex, England ; Hoboken, N.J.: Wiley), p. 2.
2. Templeton, D.M., Ariese, F., Cornelis, R., Danielsson, L.-G., Muntau, H., Van Leeuwen, H.P., and Lobinski, R. (2000). Guidelines for terms related to chemical speciation and fractionation of elements. *Pure and Applied Chemistry* 72, 1453-1470.
3. Ure, A.M., and C.M. Davidson (Eds.) (1975). Chemical Speciation in the Environment. In Chemical Speciation in the Environment. (Blackie Academic & Professional, London), pp. 160-200.
4. Hughes, K., Meek, M.E., Newhook, R., and Chan, P.K. (1995). Speciation in health risk assessments of metals: evaluation of effects associated with forms present in the environment. *Regulatory toxicology and pharmacology : RTP* 22, 213-220.
5. Brown, P.L., and Markich, S.J. (2000). Evaluation of the free ion activity model of metal-organism interaction: extension of the conceptual model. *Aquatic toxicology (Amsterdam, Netherlands)* 51, 177-194.
6. Campbell, P.G.C. (1995). Interactions between trace metals and aquatic organisms: a critique of the free-ion activity model. *IUPAC Series on Analytical and Physical Chemistry of Environmental Systems* 3, 45-102.
7. Worms, I., Simon, D.F., Hassler, C.S., and Wilkinson, K.J. (2006). Bioavailability of trace metals to aquatic microorganisms: Importance of chemical, biological and physical processes on biouptake. *Biochimie* 88, 1721-1731.
8. Morel, F. (1983). Principles of aquatic chemistry. In Principles of aquatic chemistry. (New York: J. Wiley), pp. 300-309.
9. Markich, S.J., Brown, P.L., Jeffree, R.A., and Lim, R.P. (2000). Valve movement responses of *Velesunio angasi* (Bivalvia: Hyriidae) to manganese and uranium: an exception to the free ion activity model. *Aquatic Toxicology* 51, 155-175.
10. Brown, P.L., and Markich, S.J. (2000). Evaluation of the free ion activity model of metal-organism interaction: extension of the conceptual model. *Aquatic Toxicology* 51, 177-194.
11. Errecalde, O., Seidl, M., and Campbell, P.G.C. (1998). Influence of a low molecular weight metabolite (citrate) on the toxicity of cadmium and zinc to the unicellular green alga *Selenastrum capricornutum*: an exception to the free-ion model. *Water Research* 32, 419-429.
12. Pagenkopf, G.K. (1983). Gill surface interaction model for trace-metal toxicity to fishes: role of complexation, pH, and water hardness. *Environmental Science and Technology* 17, 342-347.
13. Playle, R.C. (1998). Modeling metal interactions at fish gills. *Science of the Total Environment* 219, 147-163.
14. Di Toro, D.M., Allen, H.E., Bergman, H.L., Meyer, J.S., Paquin, P.R., and Santore, R.C. (2001). Biotic ligand model of the acute toxicity of metals. 1. Technical basis. *Environmental Toxicology and Chemistry* 20, 2383-2396.

15. Paquin, P.R., Santore, R.C., Wu, K.B., Kavvas, C.D., and Di Toro, D.M. (2000). The biotic ligand model: a model of the acute toxicity of metals to aquatic life. *Environmental Science & Policy* 3, S175-S182.
16. Van Leeuwen, H.P. (1999). Metal Speciation Dynamics and Bioavailability: Inert and Labile Complexes. *Environmental Science and Technology* 33, 3743-3748.
17. Buffle, J., Chalmers, R.A., Masson, M.R., and Midgley, D. (1988). In *Complexation reactions in aquatic systems; an analytic approach*. (Chichester, England,: Horwood.).
18. De Wit, J.C.M., Van Riemsdijk, W.H., Nederlof, M.M., Kinniburgh, D.G., and Koopal, L.K. (1990). Analysis of ion binding on humic substances and the determination of intrinsic affinity distributions. *Analytica Chimica Acta* 232, 189-207.
19. Buffle, J., Altmann, R.S., Filella, M., and Tessier, A. (1990). Complexation by natural heterogeneous compounds: Site occupation distribution functions, a normalized description of metal complexation. *Geochimica et Cosmochimica Acta* 54, 1535-1553.
20. Markich, S.J. (2002). Uranium speciation and bioavailability in aquatic systems: An overview. *TheScientificWorld* [online computer file] 2, 707-729.
21. Kawahigashi, M., Sumida, H., and Yamamoto, K. (2005). Size and shape of soil humic acids estimated by viscosity and molecular weight. *Journal of Colloid and Interface Science* 284, 463-469.
22. Mertig, M., Klemm, D., Pompe, W., Zanker, H., and Bottger, M. (1999). Scanning force microscopy of spin-coated humic acid. *Surface and Interface Analysis* 27, 426-432.
23. Filella, M., and Town, R.M. (2001). Heterogeneity and lability of Pb(II) complexation by humic substances: practical interpretation tools. *Fresenius' Journal of Analytical Chemistry* 370, 413-418.
24. Buffle, J., and Filella, M. (1995). Physico-chemical heterogeneity of natural complexants: clarification. *Analytica Chimica Acta* 313, 144-150.
25. Buffle, J., Altmann, R.S., and Filella, M. (1990). Effect of physicochemical heterogeneity of natural complexants. Part II. Buffering action and role of their background sites. *Analytica Chimica Acta* 232, 225-237.
26. Conte, P., and Piccolo, A. (1999). Conformational Arrangement of Dissolved Humic Substances. Influence of Solution Composition on Association of Humic Molecules. *Environmental Science and Technology* 33, 1682-1690.
27. Sieliechi, J.M., Lartiges, B.S., Kayem, G.J., Hupont, S., Frochot, C., Thieme, J., Ghanbaja, J., d'Espinose de la Caillerie, J.B., Barres, O., Kamga, R., Levitz, P., and Michot, L.J. (2008). Changes in humic acid conformation during coagulation with ferric chloride: Implications for drinking water treatment. *Water Research* 42, 2111-2123.
28. Yates, L.M., III, and Von Wandruszka, R. (1999). Effects of pH and metals on the surface tension of aqueous humic materials. *Soil Science Society of America Journal* 63, 1645-1649.
29. Cordfunke, E.H.P. (1970). The chemistry of uranium. Including its applications in nuclear technology. In *The chemistry of uranium*. (Amsterdam, New York,: Elsevier Pub. Co.), p. 21.

30. McDiarmid, M.A., Keogh, J.P., Hooper, F.J., McPhaul, K., Squibb, K., Kane, R., DiPino, R., Kabat, M., Kaup, B., Anderson, L., Hoover, D., Brown, L., Hamilton, M., Jacobson-Kram, D., Burrows, B., and Walsh, M. (2000). Health effects of depleted uranium on exposed Gulf War veterans. *Environmental research* 82, 168-180.
31. Abou-Donia, M.B., Dechkovskaia, A.M., Goldstein, L.B., Shah, D.U., Bullman, S.L., and Khan, W.A. (2002). Uranyl acetate-induced sensorimotor deficit and increased nitric oxide generation in the central nervous system in rats. *Pharmacology, Biochemistry and Behavior* 72, 881-890.
32. Ubios, A.M., Guglielmotti, M.B., Steimetz, T., and Cabrini, R.L. (1991). Uranium inhibits bone formation in physiologic alveolar bone modeling and remodeling. *Environmental research* 54, 17-23.
33. Aitken, M. (1999). Gulf war leaves legacy of cancer. *BMJ (Clinical research ed.)* 319, 401.
34. Hogan, A.C., van Dam, R.A., Markich, S.J., and Camilleri, C. (2005). Chronic toxicity of uranium to a tropical green alga (*Chlorella* sp.) in natural waters and the influence of dissolved organic carbon. *Aquatic Toxicology* 75, 343-353.
35. Durrance, E.M. (1986). *Radioactivity in geology : principles and applications* (E. Horwood ;Halsted Press).
36. Canadian Soil Quality Guidelines for Uranium: Environmental and Human Health (2007) (Canadian Council of Ministers of the Environment).
37. Silva, R.J., and Nitsche, H. (1995). Actinide environmental chemistry. *Radiochimica Acta* 70/71, 377-396.
38. Ebbs, S.D., Brady, D.J., and Kochian, L.V. (1998). Role of uranium speciation in the uptake and translocation of uranium by plants. *Journal of Experimental Botany* 49, 1183-1190.
39. Lenhart, J.J., Cabaniss, S.E., MacCarthy, P., and Honeyman, B.D. (2000). Uranium(VI) complexation with citric, humic and fulvic acids. *Radiochimica Acta* 88, 345-353.
40. Morel, F. (1983). Principles of aquatic chemistry. In *Principles of aquatic chemistry*. (New York: J. Wiley), pp. 266-267.
41. Baird, C. (1995). *Environmental chemistry*. (New York: W.H. Freeman), p. 16.
42. Baird, C. (1995). *Environmental chemistry*. (New York: W.H. Freeman), pp. 325-327.
43. Stumm, W., and Morgan, J.J. (1996). *Aquatic chemistry : chemical equilibria and rates in natural waters*, 3rd Edition. (New York: Wiley), pp. 148-204.
44. Atkins, P.W. (1982). *Physical chemistry*, Second Edition. (New York: W.H. Freeman), p. 226.
45. Morel, F., and Hering, J.G. (1993). *Principles and applications of aquatic chemistry*. (New York: Wiley), pp. 218-226.
46. Bidoglio, G., Cavalli, P., Grenthe, I., Omenetto, N., Qi, P., and Tanet, G. (1991). Studies on metal carbonate equilibria-Part 21. Study of the uranium(VI)-water-carbon dioxide(g) system by thermal lensing spectrophotometry. *Talanta* 38, 433-437.

47. Wang, Z., Zachara, J.M., Yantasee, W., Gassman, P.L., Liu, C., and Joly, A.G. (2004). Cryogenic Laser Induced Fluorescence Characterization of U(VI) in Hanford Vadose Zone Pore Waters. *Environmental Science and Technology* 38, 5591-5597.
48. Zhang, H., and Davison, W. (1995). Performance Characteristics of Diffusion Gradients in Thin Films for the in Situ Measurement of Trace Metals in Aqueous Solution. *Analytical Chemistry* 67, 3391-3400.
49. Lehto, N.J., Davison, W., Zhang, H., and Tych, W. (2006). An Evaluation of DGT Performance Using a Dynamic Numerical Model. *Environ. Sci. Technol.* 40, 6368-6376.
50. Lehto, N.J., Davison, W., Zhang, H., and Tych, W. (2006). Analysis of Micro-Nutrient Behaviour in the Rhizosphere using a DGT Parameterised Dynamic Plant Uptake Model. *Plant and Soil* 282, 227-238.
51. Koryta, J.r., Dvorák, J.r., and Kavan, L. (1993). Principles of electrochemistry. In *Principles of electrochemistry*, 2nd Edition. (Chichester ; New York: Wiley), pp. 80-81.
52. Gustafsson, J.P. (2001). Modeling the Acid-Base Properties and Metal Complexation of Humic Substances with the Stockholm Humic Model. *Journal of Colloid and Interface Science* 244, 102-112.

Chapter 2

Diffusive gradients in thin-films (DGT)

2.1 Theory

2.1.1 Principle of DGT

DGT is a speciation tool[1], consisting of a diffusive layer and a binding layer(Figure 2.1) [2]. When DGT is deployed in aqueous media, the metal species (free metal ions and metal complexes), which diffuse through the diffusive layer, either react with the binding layer directly (Adjunctive Pathway), or react with the binding layer after dissociation (Disjunctive Pathway).

Figure 2.1 DGT device assembly (adapted from Zhang et. al. 1995) [2]

When a steady-state diffusion gradient is established, the flux of metal species can be expressed as[1]:

$$M = J \times A \times t \quad (2.1)$$

Therefore,

$$J = M / At \quad (2.2)$$

where J is the steady-state flux of metal species, M is the accumulated metal mass on the binding layer, A is the surface area of the window of diffusive layer and t is the experimental time. (Figure 2.2).

Figure 2.2 A schematic diagram of the principle of DGT[2]

If the thickness Δx , of Diffusive Boundary Layer (DBL) is small compared to the thickness of diffusive gel layer [2], the flux (J) of metal species that diffuses through the diffusive layer can be expressed as follows, based on the Fick's first law of diffusion:

$$J = D(c_b - c') / \Delta g \quad (2.3)$$

where D is the diffusion coefficient in the diffusive layer, Δg is the thickness of the diffusive layer, c_b is the concentration of the metal species in the bulk solution and c' is the concentration of metal species on the surface of the binding layer.

If the free metal ions rapidly react with the binding layer forming a strong complex, and the binding layer is not saturated during the experiment, the c' is effectively zero. Therefore, Eq. 2.3 can be simplified to

$$J = Dc_b / \Delta g \quad (2.4)$$

Combining Eqs. (2.2) and (2.4), and gets

$$M = \frac{tA}{\Delta g} Dc_b \quad (2.5)$$

and
$$c_b = M\Delta g / DtA \quad (2.6)$$

What DGT really measures in natural surface freshwaters is the flux, that is, the integration of the supply of metal species in a given time across a given surface area. This rate of the supply from solution depends on both the diffusion rate of the species in the diffusive layer and the kinetics reaction rate of the metal species in DGT binding layer, so that DGT measures the DGT-labile species, which reflect both the mobility and the lability properties of the metal species. By simply controlling the mass transport to a binding layer, such as Chelex-100 resin layer, it is possible to quantify the accumulated metal (bound by the binding layer) in terms of a measured flux. Since DGT is intended to be deployed in natural waters, it is necessary to consider the following characteristics of natural waters vis-à-vis those of the DGT:

- 1) Natural waters are open and dynamic systems, which can exchange matters and energy with their surroundings.[4].
- 2) The driving force of mass flux is the chemical potential difference (concentration difference) between the metal species in the surface freshwaters and that on the surface of binding layer, which is controlled by the binding kinetics of the binding layer. Mass transport in diffusive layer is constrained by using a sufficiently thick well-defined diffusive layer.

- 3) Mass of metal accumulated by DGT binding layers is the sum-total of the contributions of all metal species integrated over the deployment time. The contribution of species depends both on the DGT detection window and the composition of the natural waters (concentration of the species, pH, ionic strength, concentration of competing metals, and major ion concentrations) [5].

The objective of this thesis is to investigate uranium speciation in aqueous model solutions and surface freshwaters, and to study the effects of other parameters such as pH, ionic strength, inorganic complexant (carbonate) on uranium speciation, and the competition between other trace metal (such as copper) and uranium for binding with FA and HA.

2.1.2 Diffusive layer

Diffusive layer controls the flux of metal species. The requirements for DGT diffusive layer are:

- 1) During the deployment time period, the structure of diffusive layer must remain stable, and the diffusion coefficients of metal ions in diffusive layer must remain constant.
- 2) No adsorption of metal ions by the diffusive layer
- 3) The pore size of diffusive layer is large enough for all the metal species.

Polyacrylamide gel, which consists of an acrylamide monomer cross-linked with an agarose derivative, has been chosen as the first candidate of the diffusive layer[2]. Agarose gel[6] and dialysis membrane[3, 7] has been used by other workers as diffusive layer, recently.

Polyacrylamide gel that consists of an acrylamide monomer, cross-linked with bis-acrylamide, has been widely used in polyacrylamide gel electrophoresis (PAGE) to separate proteins.

2.1.3 DGT binding layer

The requirements for DGT binding layer are:

- 1) Fast and strong, irreversible binding with the metal ions
- 2) Large capacity for metal accumulation and never to be saturated during the deployment of the DGT
- 3) Stable for the conditions of the natural waters (pH, ionic strength, temperature...)

Chelex-100, which binds most of trace metals strongly and fast, has been traditionally chosen as the binding gel layer used in the DGT experiment. An ammonium molybdophosphate (AMP) binding agent was used by other workers for the measurement of Cs[8]. Ion-exchange filter membrane DE81 was used for uranium speciation study[9], as also was liquid binding phase poly(4-styrenesulfonate) (PSS) for DGT studies[3, 7] (Figure 2.3).

Figure 2.3 Diagram of poly(4-styrenesulfonate) (PSS) liquid binding phase DGT device[3]

2.1.4 DGT-labile species

DGT measures the species which can diffuse through the DGT diffusive layers and can be bound by the DGT binding layers. As shown in Figure 2.4, the concentration of metal species on the surface of binding layers is not always zero. That means only a part of metal species reacts with DGT binding layers during the experimental timescale. These metal species are operationally defined as ‘DGT-labile species’. The DGT-labile species and the effect of the speciation parameters on the DGT-labile species have been discussed in Chapter 5.

Figure 2.4 Metal-ligand complex (ML) in DGT experiment [2]
 (a) fully labile (b) totally inert (c) partially labile

2.1.5 Applications of DGT

The applications of DGT include:

- 1) *in-situ* analysis in waters, sediments and soils: DGT promises to be a very good *in-situ* tool for the study of metal speciation. Zhang and Davison have done the definitive work on DGT *in-situ* analysis of trace metal speciation in natural waters[10-12], sediments[11, 13] and soils[14, 15]. Harper et al. [16] used two-

dimensional numerical models of DGT deployments in horizontally uniform sediments to study the metal speciation in pore waters in sediments.

- 2) Pre-concentration of trace metals: if the concentration of a trace metal is too low, DGT's intrinsic pre-concentration mechanism becomes important for the determination of that trace metal. French et al. [17] found that the use of DGT in combination with ICP-MS to determine ^{99}Tc offered a lower detection limit than other methods.
- 3) Kinetic studies: many kinetic studies have been done using DGT. Scally et al. determined the diffusion coefficient of the free metal ions and metal-ligand complexes of Pb, Ni, Cu and Cd in diffusive gel layer[18] and have studied the dissociation kinetics of Ni and Cu complexes in solutions[19].
- 4) Metalloid speciation analysis: Teasdale et al.[20] developed the DGT method for the measurement of dissolved sulfide. Zhang et al. [21] successfully determined dissolved phosphorus in natural waters using DGT.
- 5) Water contamination monitoring: Buzier et al.[22] used DGT to sample metal species in wastewater and obtain information on the speciation of copper and cadmium in diluted and spiked filtered wastewaters. Yapici et al.[23] used DGT to study the metal speciation in aqueous mine effluents.

2.2 Experimental

In this section, the experimental procedures of DGT preparation, deployment and uranium determination are presented.

2.2.1 Reagents

All sample solutions were prepared with deionized water of resistivity of 18.2 M Ω -cm, obtained direct from a NANOpure Diamond Ultrapure Water System (Barnstead, USA). All reagents used for the preparation of polyacrylamide gel and Chelex-100 gel were of analytical grade. The acrylamide monomer solution (40%) and Chelex 100 resin of 200–400 mesh were obtained from Bio-Rad. Ammonium persulphate and N,N,N',N'-tetramethylethylenediamine were obtained from Fisher Scientific, Inc., Canada. Agarose derived crosslinker (2%) and the DGT holders were purchased from DGT Research Ltd., UK. Cellulose nitrate filter membrane (0.45 μ m) was purchased from Fisher Scientific, Canada. Concentrated Optima nitric acid (Fisher Scientific) was used for preparation of all acidic solutions. All experiments were carried out in high-density polypropylene vessels.

2.2.2 Preparation of gel for DGT

The polyacrylamide gel and Chelex-100 resin gel were prepared following the procedures described earlier[2], and the Users' Guide prepared by DGT Research Ltd. The thickness and the diameter of the diffusion gel layer were 0.040 cm and 2.5 cm, respectively. For making 10 ml gel solution, mix 1.5 ml DGT gel cross-linker and 4.75 ml deionised water

together were mixed in a clean plastic bottle; then, 3.75 ml acrylamide solution (40%) was added into the above solution.

Preparation of Diffusive Gel:

Glass plates and plastic spacers were washed using nitric acid (5% v/v) and then wiped dry with clean tissue papers. A spacer (0.4 mm) was placed round three edges of glass plate and then two glass plates were clipped together. 5 ml of gel solution was pipetted into a tube and add 35 μ l of ammonium persulphate solution (10% v/v) was added to the above solution followed by 12.5 μ l of TEMED solution. The solution was pipetted in between the two glass plates. The assembly of the two glass plates was maintained at about 40°C for 1 hour until the gel was completely set. The assembly was prised open and the gels were washed using deionized water.

Preparation of binding resin gel:

5 ml of gel solution was pipetted into a tube; 2g Chelex-100 resin was added to the above solution and the solution was mixed. 30 μ l of ammonium persulphate solution and 12.5 μ l of TEMED were added into the above solution. The solution was well mixed and then pipetted immediately in between two glass plates. The assembly was maintained at about 40°C for 1 hour until the gel was completely set. The assembly was prised open and the gels were washed using deionized water.

The DGT diffusion gel and Chelex-100 binding gel were cut 2.5 cm in diameter.

2.2.3 Assembly and deployment of DGT

As shown in Figure 2.1, DGT binding layer (Chelex-100 gel or ion-exchange filter paper), the DGT diffusive layer and the protective layer of cellulose membrane were placed on the piston in sequence. The outer sleeve with window (2 cm in diameter) was capped on the piston. The DGT devices were tied to a fishing string and then suspended in aqueous model solutions or deployed in natural surface freshwaters. After experiment, the DGT binding layers were taken out from the piston and the accumulated metal was eluted by HNO_3 (20% v/v).

2.2.4 Determination of uranium concentration

To determine uranium concentration, Inductively Coupled Plasma Mass Spectrometry (ICP-MS) and Kinetic Phosphorescence Analyzer (KPA) were used. PerkinElmer Elan 6100 DRC ICP-MS was used to determine uranium in natural waters and in the eluted solution of the DGT-accumulated metal. The operational parameters of Elan 6100 DRC ICP-MS were presented in Table 2.1.

Table 2.1 Instrument operating conditions for Elan 6100 DRC ICP-MS

Elan 6100 DRC ICP-MS	
RF power (kW)	1.1
Carrier argon gas flow rate (L min^{-1})	0.8
Auxiliary argon gas flow rate (L min^{-1})	1
Dwell time (ms)	50
Scan mode	peak hop
Signal measurement	counts s^{-1}
Points/spectral peak	1
Resolution	normal

A Kinetic Phosphorescence Analyzer, KPA-10 (ChemChek Instruments, Inc.), was used to determine uranium concentration in the eluted solution of DGT binding layers. 1.5 mL UraplexTM (ChemChek Instruments, Inc) solution was added to each sample to enhance the uranyl phosphorescence.[24-27]

2.2.5 QA/QC

A uranium analytical standard (1000 mg L⁻¹, SPEX Inc., USA) was used to prepare the external calibration standards and the linearity of the calibration curve within the range of 0 to 100 µg L⁻¹ was close to 1 (>0.99). Certified Reference Materials (CRM), (CANMET-STSD-2, CANMET-STSD-4, IAEA-SL-1 and SLRS-4), were analyzed as quality control samples to ensure the accuracy and precision of the uranium calibration standards. The measured CRM values agreed with the certified values as presented in Table 2.2.

Quality control samples, which contain known concentration of analyte in a blank matrix or a similar matrix as the unknown[28], were determined in every set of samples. SLRS-4 was used as quality control sample when natural water samples were analyzed. Uranium standard samples containing a known concentration (e.g. 5 µg L⁻¹) were used as quality control samples for routine analysis. All measurements were done in triplicate. If the measured values of quality control samples differed from the known values by > 10%, the calibration curve and the prior set of samples were re-analyzed. The relative standard deviation of replicate determination was typically less than 5%. Blanks and calibration standards were re-determined every two hours to monitor the instrument performance.

Kinetic Phosphorescence Analyzer (KPA) and ICP-MS produce similar results with the analytical standards and Chelex-100 DGT samples (Figure 2.5). Standard addition method was used for some samples (e.g. uranium-humic acid model solutions) to avoid the matrix effect.

Figure 2.5 Comparison of uranium concentrations in DGT samples determined using KPA and ICP-MS.

Table 2.2 Concentrations of uranium in Certified Reference Materials and their certified values. (Determined using ICP-MS)

SRM	Description	Method	Uranium concentration (measured)	Uranium concentration (certified value)
STSD-2	Stream sediment	Digestion and standard addition	$17.9 \pm 0.2 \text{ mg kg}^{-1}$	18.6 mg kg^{-1}
STSD-4	Stream sediment	Digestion and standard addition	$3.0 \pm 0.3 \text{ mg kg}^{-1}$	3 mg kg^{-1}
IAEA-SL-1	Lake sediment	Digestion and standard addition	$4.4 \pm 0.4 \text{ mg kg}^{-1}$	$3.69\text{--}4.35^* \text{ mg kg}^{-1}$
SLRS-4	River water	Direct determination	$0.049 \pm 0.002 \text{ } \mu\text{g L}^{-1}$	$0.050 \pm 0.003 \text{ } \mu\text{g L}^{-1}$

The uncertainties represent 95 percent confidence limits for an individual subsample.

*95% Confidence Interval

2.3 References

1. INAP (March 2002). Diffusive Gradients in Thin-films (DGT) - A Technique for Determining Bioavailable Metal Concentrations (The International Network for Acid Prevention).
2. Zhang, H., and Davison, W. (1995). Performance Characteristics of Diffusion Gradients in Thin Films for the in Situ Measurement of Trace Metals in Aqueous Solution. *Analytical Chemistry* 67, 3391-3400.
3. Li, W., Teasdale, P.R., Zhang, S., John, R., and Zhao, H. (2003). Application of a Poly(4-styrenesulfonate) Liquid Binding Layer for Measurement of Cu²⁺ and Cd²⁺ with the Diffusive Gradients in Thin-Films Technique. *Anal. Chem.* 75, 2578-2583.
4. Stumm, W., and Morgan, J.J. (1996). Aquatic chemistry : chemical equilibria and rates in natural waters. In *Aquatic chemistry : chemical equilibria and rates in natural waters*, 3rd Edition. (New York: Wiley), pp. 2-20.
5. Tessier, A., and Turner, D.R. (1995). Metal speciation and bioavailability in aquatic systems. In *IUPAC series on analytical and physical chemistry of environmental systems* ;. pp. 219-240, John Wiley: New York.
6. Docekalova, H., and Divis, P. (2005). Application of diffusive gradient in thin films technique (DGT) to measurement of mercury in aquatic systems. *Talanta* 65, 1174-1178.
7. Li, W., Zhao, H., Teasdale, P.R., John, R., and Wang, F. (2005). Metal speciation measurement by diffusive gradients in thin films technique with different binding phases. *Anal. Chim. Acta* 533, 193-202.
8. Murdock, C., Kelly, M., Chang, L.-Y., Davison, W., and Zhang, H. (2001). DGT as an in Situ Tool for Measuring Radiocesium in Natural Waters. *Environ. Sci. Technol.* 35, 4530-4535.
9. Li, W., Zhao, J., Li, C., Kiser, S., and Cornett, R.J. (2006). Speciation measurements of uranium in alkaline waters using diffusive gradients in thin films technique. *Anal. Chim. Acta* 575, 274-280.
10. Davison, W., and Zhang, H. (1994). In situ speciation measurements of trace components in natural waters using thin-film gels. *Nature (London, United Kingdom)* 367, 546-548.
11. Davison, W., and Zhang, H. (2000). In situ measurement of labile species in water and sediments using DGT. *Ocean Sci. Technol.* 1, 283-302.
12. Warnken, K.W., Davison, W., and Zhang, H. (2008). Interpretation of In Situ Speciation Measurements of Inorganic and Organically Complexed Trace Metals in Freshwater by DGT. *Environmental Science & Technology* 42, 6903-6909.
13. Tankere-Muller, S., Zhang, H., Davison, W., Finke, N., Larsen, O., Stahl, H., and Glud, R.N. (2007). Fine scale remobilization of Fe, Mn, Co, Ni, Cu and Cd in contaminated marine sediment. *Mar. Chem.* 106, 192-207.
14. Hooda, P.S., and Zhang, H. (2008). DGT measurements to predict metal bioavailability in soils. *Developments in Soil Science* 32, 169-185.
15. Davison, W., Zhang, H., and Miller, S. (1997). In situ procedures for measuring chemical speciation and availability of trace metals in soils and sediments. *Colloq. - Inst. Natl. Rech. Agron.* 85, 55-67.

16. Harper, M.P., Davison, W., and Tych, W. (1999). Estimation of pore water concentrations from DGT profiles: a modeling approach. *Aquat. Geochem.* 5, 337-355.
17. French, M.A., Zhang, H., Pates, J.M., Bryan, S.E., and Wilson, R.C. (2005). Development and Performance of the Diffusive Gradients in Thin-Films Technique for the Measurement of Technetium-99 in Seawater. *Anal. Chem.* 77, 135-139.
18. Scally, S., Davison, W., and Zhang, H. (2006). Diffusion coefficients of metals and metal complexes in hydrogels used in diffusive gradients in thin films. *Anal. Chim. Acta* 558, 222-229.
19. Scally, S., Davison, W., and Zhang, H. (2003). In Situ Measurements of Dissociation Kinetics and Labilities of Metal Complexes in Solution Using DGT. *Environ. Sci. Technol.* 37, 1379-1384.
20. Teasdale, P.R., Hayward, S., and Davison, W. (1999). In situ, High-Resolution Measurement of Dissolved Sulfide Using Diffusive Gradients in Thin Films with Computer-Imaging Densitometry. *Anal. Chem.* 71, 2186-2191.
21. Zhang, H., Davison, W., Gadi, R., and Kobayashi, T. (1998). In situ measurement of dissolved phosphorus in natural waters using DGT. *Anal. Chim. Acta* 370, 29-38.
22. Buzier, R., Tusseau-Vuillemin, M.-H., and Mouchel, J.-M. (2006). Evaluation of DGT as a metal speciation tool in wastewater. *Sci. Total Environ.* 358, 277-285.
23. Yapici, T., Fasfous, I.I., Murimboh, J., and Chakrabarti, C.L. (2008). Investigation of DGT as a metal speciation technique for municipal wastes and aqueous mine effluents. *Analytica Chimica Acta* 622, 70-76.
24. Ejniak, J.W., Hamilton, M.M., Adams, P.R., and Carmichael, A.J. (2000). Optimal sample preparation conditions for the determination of uranium in biological samples by kinetic phosphorescence analysis (KPA). *Journal of Pharmaceutical and Biomedical Analysis* 24, 227-235.
25. Elliston, J.T., Glover, S.E., and Filby, R.H. (2005). Comparison of direct kinetic phosphorescence analysis and recovery corrected kinetic phosphorescence analysis for the determination of natural uranium in human tissues. *Journal of Radioanalytical and Nuclear Chemistry* 263, 301-306.
26. Hedaya, M.A., Birkenfeld, H.P., and Kathren, R.L. (1997). A sensitive method for the determination of uranium in biological samples utilizing kinetic phosphorescence analysis (KPA). *Journal of Pharmaceutical and Biomedical Analysis* 15, 1157-1165.
27. Moore, L.L., and Williams, R.L. (1992). A rapid method for determining nanogram quantities of uranium in urine using the kinetic phosphorescence analyzer. *Journal of Radioanalytical and Nuclear Chemistry* 156, 223-233.
28. Harris, D.C. (2003). *Quantitative chemical analysis*, 6th Edition. (New York: W.H. Freeman), p. 733.

Chapter 3

**Diffusion coefficients of uranium
species**

3.1 Introduction

Diffusion is a passive transport process, which is driven by concentration gradients[1]. As defined by Crank (1956), “diffusion is the process by which matter is transported from one part of a system to another as a result of random molecular motions” [2, 3]. As presented in Eq. 3.1 (Fick’s first law of diffusion), the flux of matter (J), which diffuses parallel to the z-axis, is proportional to the concentration gradient,

$$J = -D \frac{dc}{dz} \quad (3.1)$$

where J is flux, D is diffusion coefficient; c is the concentration of metal ions and z is the distance, dc/dz is the concentration gradient. The negative sign of diffusion coefficient signifies that the flux J is down a concentration gradient, from high to low[4].

3.1.1 Thermodynamic view of diffusion

At constant temperature (T) and pressure (p), the thermodynamic force, $\mathcal{F}$, of a concentration gradient is written as follows[5]:

$$\mathcal{F} = -\left(\frac{\partial \mu}{\partial z}\right)_{p,T} \quad (3.2)$$

where μ is chemical potential, z is the distance.

In a solution in which the activity of the solute is a, the chemical potential $\mu = \mu^0 + RT \ln a$, and the Eq. 3.2 can be written as

$$\mathcal{F} = -RT \left(\frac{\partial \ln a}{\partial z}\right)_{p,T} \quad (3.3)$$

If the solution is ideal, a can be replaced by the molar concentration c, and then the Eq. 3.3 can be written as:

$$\mathcal{F} = -\frac{RT}{c} \left(\frac{\partial \ln c}{\partial z}\right)_{p,T} \quad (3.4)$$

The flux J is related to the drift speed as

$$J = sc \quad (3.5)$$

where s is the speed of the mass transport. Therefore,

$$sc = -D \frac{dc}{dz} \quad (3.6)$$

Eq. 3.6 can be expressed in terms of $\mathcal{F}$ by using Eq. 3.4 as:

$$s = -\frac{D}{c} \frac{dc}{dz} = \frac{D\mathcal{F}}{RT} \quad (3.7)$$

3.1.2 Diffusion coefficient and mobility

In the case of an ion in solution under a electric field of strength E , the drift speed is known as $s=uE$, and the drift force, $\mathcal{F}$, is zFE , where u is mobility of an ion, F is the

Faraday constant ($F=N_Ae$). Therefore, Eq. 3.7 can be written as[5]:

$$uE = \frac{zFED}{RT} \quad (3.8)$$

and hence

$$u = \frac{zFD}{RT} \quad (3.9)$$

This equation is known as the **Einstein relation**, relating the diffusion coefficient to ionic mobility:

$$D = \frac{uRT}{zF} \quad (3.10)$$

The mobility of an ion is defined as

$$u = \frac{ze}{6\pi\eta a} \quad (3.11)$$

where η is the viscosity of the medium, a is the radius of an ion. Combining Eq. 3.10 and Eq. 3.11, using $eR/F=k$, gives **Stoke-Einstein equation**

$$D = \frac{kT}{6\pi\eta a} \quad (3.12)$$

where k is boltzmann constant.

In a given medium, if pressure remains constant, the diffusion coefficient of a particle is a function of temperature T .

3.1.3 Diffusion coefficient and temperature

The temperature dependence of diffusion coefficients is linked to the viscosity of medium, and the absolute temperature, T , by the **Stoke-Einstein equation**:

$$\frac{D_1\eta_1}{T_1} = \frac{D_2\eta_2}{T_2} \quad (3.13)$$

As the temperature dependence of the viscosity of water is well established[6], the diffusion coefficient of ions in water at different temperatures can be calculated. In practice, the viscosity of water is represented by Eq. 3.14[7], where t is temperature (in °C).

$$\log \frac{\eta_{25}}{\eta_t} = \frac{1.37023(t - 25) + 8.36 \times 10^{-4}(t - 25)^2}{109 + t} \quad (3.14)$$

And the diffusion coefficient at any temperature, D_T , can be calculated by Eq. 3.15, where D_{25} is the diffusion coefficient of ions in water at 25°C[7].

$$\log D_t = \frac{1.37023(t-25) + 8.36 \times 10^{-4}(t-25)^2}{109+t} + \log \frac{D_{25}(273+t)}{298} \quad (3.15)$$

3.1.4 Statistical view of diffusion

If the diffusion process is assumed as one-dimensional random walk, which means all particles travel only along a straight line and for each step pass through a same distance, λ , in a same time, τ , the probability of a particle being at a distance x from the origin point after a time t is[5]:

$$P = \left(\frac{2\tau}{\pi t}\right)^{1/2} e^{-x^2 \tau / 2t \lambda^2} \quad (3.16)$$

The diffusion coefficient can be written as **Einstein-Smoluchowski equation**:

$$D = \frac{\lambda^2}{2\tau} \quad (3.17)$$

If we simplify the diffusion process in polyacrylamide gel as one step jump (passing through a distance Δg in a time Δt , the diffusion time can be calculated using Eq. 3.18[7]

$$\Delta t = \frac{\Delta g^2}{2D} \quad (3.18)$$

The metal complexes may dissociate during the diffusion time in the diffusive gel layer[8]. According to Eq. 3.18, if the diffusion coefficient of one metal species is $1 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$, Δg is 0.04 cm; the diffusion time Δt is 800s, which is long enough for some metal complexes to dissociate.

3.1.5 Types of diffusion modes

Four types of diffusion have been studied[3] using the diffusion cell method, as shown in Figure 3.1.

1. Self-diffusion: according to the IUPAC Compendium of Chemical Terminology (1997), self-diffusion coefficient is the diffusion coefficient of the species when the chemical potential gradient equals zero.
2. Tracer diffusion: in diffusion cell experiment, the two compartments contain the same solution and a tracer amount of a radioactive isotope of a given ion is spiked in one of the compartments.
3. Salt diffusion: the concentration gradients of the diffusing cation and anion have the same magnitude.
4. Counter diffusion: the ions are exchangeable in salt diffusion in two compartments.

In this study, since the uranium concentration is at very low level compared to the concentration of NaNO_3 , a “tracer diffusion mode” can be used.

Figure 3.1 Diagrams of the diffusion modes[3]

3.2 Experimental

3.2.1 Reagents

All the solutions were prepared using deionized water. A 1000 mg L^{-1} uranium standard solution was purchased from SPEX CertiPrep Inc., US, and used as stock solutions for the experiments and as calibration standards for the determination of uranium. Concentrated optima nitric acid (Fisher Scientific) was used for all acidic solution preparation. Sodium carbonate and sodium bicarbonate were purchased from Fisher Scientific Inc., Canada. Humic acid was obtained from Dr. Les Evens, the University of Guelph, ON, Canada.

3.2.2 Preparation of diffusive gel

The polyacryamide (PAM) diffusive gel was prepared as described in Chapter 2.

3.2.3 Determination of diffusion coefficient

Diffusion coefficients of uranium in PAM gel were measured according to the previously described method by Zhang et al[9]. A polyacrylic cell (Figure 3.2) with two compartments was used. One compartment (A) initially contained 600-800 mL of 1.0 mg L⁻¹ uranium solution (source solution) and the other compartment (B) initially contained receiver solution of the same volume as the compartment A with no added uranium. The ionic strengths of the solutions in both compartments were adjusted to 0.01 M by the addition of NaNO₃ (1 mol L⁻¹). The pH in both the source and the receiver solution was adjusted from 3 to 9. The overall diffusion coefficient D_U (cm²s⁻¹) can be calculated using Eq. 3.19

$$D_U = \frac{s \times \Delta g \times V_R}{A \times c_s} \quad (3.19)$$

where s is the slope of the curve of concentration in the receiver solution versus time, Δg is the thickness of the diffusive gel, V_R is the volume of the receiver solution, A is the exposed area of the diffusive gel, c_s is the concentration of the source solution. The model solutions of uranium- sodium carbonate, uranium-sodium bicarbonate and uranium-humic acid were also tested as source solution.

The concentrations of CO₃²⁻ and HCO₃⁻ (inorganic carbon) and the concentrations of humic acid (Dissolved Organic Carbon) in the receiver solutions were determined using

Shimadzu Total Organic Carbon Analyzer (TOC-VCPH). The diffusion coefficients of CO_3^{2-} , HCO_3^- and HA were also calculated using Eq. 3.19

The stock total carbonate (TC) standard solution were prepared by dissolving 2.125 g potassium hydrogen phthalate that previously dried at 105-120 °C for about 1 hour and cooled in a desiccator in 1 L ultrapure water. The stock IC standard solution were prepared by dissolving 3.50 g dried sodium hydrogen carbonate and 4.41 sodium carbonate in 1 L ultrapure water. The calibration standards for determination of DOC and IC were prepared using the stock solutions. DOC (humic acid) and IC standard samples containing a known concentration were used as quality control samples for DOC and IC analysis. All measurements were done in triplicate.

Figure 3.2 Diagram of diffusion cell[9]

3.3 Results and discussion

3.3.1 Diffusion coefficient of uranium

The diffusion coefficient of a specific uranium species is dependent on temperature only, as discussed earlier, and is independent of pH, ionic strength and other speciation parameters. However, the overall (apparent) diffusion coefficient, D_U , varies with the speciation parameters in the diffusion cell experiment because the distribution of species varies with speciation parameters. D_U is a weighted average of the diffusion coefficients of all uranium species as shown by Eq. 3.20; the weighting factor is the percentage of each individual uranium species.

$$D_U = \frac{\sum_i D_{Ui} c_{Ui}}{\sum_i c_{Ui}} \quad (3.20)$$

where D_{Ui} is the diffusion coefficient of the uranium species, c_{Ui} is the concentration of the uranium species.

3.3.2 Donnan potential and ionic strength

The Donnan potential in charged gels have been studied [10, 11]. Scally et. al.[12] reported that the diffusion coefficients of Pb, Ni, Cu and Cd at 0.1 mmol L⁻¹ ionic strength were 50% lower than those at higher ionic strengths. Therefore the Donnan potential affects the diffusion of metal species at very low ionic strength. Since the ionic strength in natural waters is usually higher than 1 mmol L⁻¹, the effect of Donnan potential on the DGT experiment in natural waters is not significant.

3.3.3 The effect of pH on the overall diffusion coefficient of uranium

The diffusion coefficient of uranium varies with the change in pH and concentration, probably because of the changes in the uranium speciation (Figure 3.3). At lower pHs, the uranium exists as uranyl ion (UO_2^{2+}), which has a higher diffusion coefficient than other the uranium species. Garmo et al. [13] have reported that the DGT-estimated diffusion coefficient of U is $4.22 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ at pH 4.7-5.9 in mixed test solutions containing 55 elements; this value is close to the value of diffusion coefficients of uranyl ion in this work. The distribution of uranium species in source solutions, in which CO_3^{2-} is 1 mg L^{-1} is presented in Table 3.1. As the pH is increased to 5, the speciation of uranium in source solutions becomes complicated because of the formation of U-OH species. The results show that at low pH the distribution of uranium is almost the same as that without considering the atmospheric CO_2 (Appendix A). At pH 7 to 8, the uranium species with bigger molecular size (e.g., $(\text{UO}_2)_2\text{CO}_3(\text{OH})_3^-$) is the dominant species, therefore the overall diffusion coefficient decreases. As pH increases, the small molecular uranium species increase, resulting in the increase of the overall diffusion coefficient of uranium at pH 9. The atmospheric CO_2 effect is more significant at higher pH since the acid-base reaction increases the absorption of CO_2 .

In natural waters systems, the concentration of uranium is at trace levels ($\mu\text{g L}^{-1}$), which is much lower than that in source solutions used in this work. The distribution of uranium species at pH 8 when uranium concentration is 1, 10 and $100 \mu\text{g L}^{-1}$ is presented in Table 3.2. Those results indicate that the total uranium concentration influences the distribution of uranium species and consequently affects the overall diffusion coefficient of uranium. Hence the overall diffusion coefficient of uranium obtained from the diffusion cell

experiment is not equal to the diffusion coefficient of uranium in real natural water samples, but provides a rough approximation of the real diffusion coefficients.

Figure 3.3 Overall diffusion coefficients of uranium in different pHs. NaNO_3 concentration in source solutions: 0.01 mol L^{-1} . Uranium concentration in source solutions:
 ▲: 1 mg L^{-1} and ■: 10 mg L^{-1}

Furthermore, in natural waters, the inorganic and organic ligands profoundly affect the uranium speciation, resulting in the variation of overall uranium diffusion coefficient. To investigate the effect of inorganic and organic ligands on the overall diffusion coefficient of uranium, U-carbonate, U-bicarbonate and U-humic acid model solutions have been tested in this study.

Table 3.1

Overall diffusion coefficient of uranium D_U and percentage distribution of uranium species in the source solutions at different pHs, calculated using the computer program Visual Minteq. The concentrations of uranium in the source solutions, c_s , are 1 and 10 mg L⁻¹. Assuming the concentration of CO₃²⁻ is 1 mg L⁻¹.

		Percentage distribution of uranium species in source solutions (%) [*]								
c_s (mg L ⁻¹)	pH	D_U (10 ⁻⁶ cm ² s ⁻¹)	UO ₂ ²⁺	UO ₂ OH ⁺	(UO ₂) ₂ (OH) ₂ ²⁺	(UO ₂) ₃ (OH) ₃ ⁺	(UO ₂) ₂ CO ₃ (OH) ₃ ⁻	(UO ₂) ₄ (OH) ₇ ⁺	(UO ₂) ₃ (OH) ₇ ⁻	UO ₂ (OH) ₃ ⁻
1	3	4.8	98.3	0.4						
	5	2.6	64.8	26.7	4.9	1.0				
	7	1.5	0.1	2.4		7.0	85.3			0.2
	8	2.4		0.2			93.8			2.3
	9	3.6					75.5			20.8
10	2	5.0	99.5	0.4						
	5	1.7	39.2	16.2	18.1	22.4	0.2	1.3		
	7	1.2		0.9	0.1	34.5	52.5	10.6	0.1	0.1
	9	1.7				0.8	66.9	0.3	18.8	11.7

^{*}The linearity of the curve of uranium concentration versus time, which was used to determine diffusion coefficients, is high than 95%. The uranium speciation was calculated using Visual Minteq. Standard deviation is not shown in this table.

Table 3.2

The percentage distribution of uranium species in the source solutions at pH 8, calculated using the computer program Visual Minteq. The concentrations of uranium in the source solutions, c_s , are 1, 10 and 100 $\mu\text{g L}^{-1}$. Assuming the concentration of CO_3^{2-} is 1 mg L^{-1} .

c_s ($\mu\text{g L}^{-1}$)	Percentage distribution of uranium species in source solutions (%) [*]					
	$\text{UO}_2(\text{CO}_3)_2^{2-}$	UO_2OH^+	$\text{UO}_2(\text{OH})_3^-$	$\text{UO}_2(\text{OH})_2$ (aq)	$(\text{UO}_2)_2\text{CO}_3(\text{OH})_3^-$	UO_2CO_3 (aq)
1	1.3	3.1	30.7	38.5	22.9	3.6
10	0.7	1.6	15.7	19.8	60.4	1.8
100	0.2	0.6	5.9	7.4	84.9	0.7
						0.1

^{*}The uranium speciation was calculated using Visual Minteq. Standard deviation is not shown in this table.

3.3.4 Overall diffusion coefficients of uranium in the carbonate and the bicarbonate model solutions

The uranium concentration in the receiver solution as a function of experimental time is presented in Figure 3.4 and 3.5. The overall diffusion coefficients of uranium in sodium carbonate and sodium bicarbonate solution are $2.7 \pm 0.6 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ and $2.3 \pm 0.2 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ respectively, determined using the diffusion cell method. Perry et al. [14] have determined the diffusion coefficient of uranium in carbonate solution using potentiostatic method, and have reported the value of diffusion coefficient as $3 \pm 0.7 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$, which compares well with our result in the sodium carbonate model solution. The diffusion coefficients of uranium in the two model solutions are close to the diffusion coefficients of 1 mg L^{-1} uranium at pH 5 and 8. The pH of sodium carbonate solutions was about 11, whereas the pH of sodium bicarbonate solutions was about 8.

The diffusion coefficient of carbonate and bicarbonate ions has been also determined. As shown in Figure 3.6 and 3.7, the diffusion rate of carbonate ion in polyacrylamide gel ($1.6 \pm 0.1 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$) is faster than that of bicarbonate ion ($4.9 \pm 0.2 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$). The result does not agree with the self-diffusion coefficient of carbonate ion ($0.804 \pm 0.008 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$) and bicarbonate ion ($1.09 \pm 0.015 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$) in water [15, 16], indicating the polyacrylamide gel might affect the diffusion of carbonate and bicarbonate ions. The difference of the diffusion coefficients between carbonate and bicarbonate does not affect the diffusion coefficient of uranium in the model solutions, because the distribution of the uranium species in the two model solutions are almost same.

Figure 3.4 Uranium concentration in the receiver solution as a function of experimental time. Source solution: uranium concentration 1 mg L^{-1} , Na_2CO_3 1000 mg L^{-1} .

Figure 3.5 Uranium concentration in the receiver solution as a function of experimental time. Source solution: uranium concentration 1 mg L^{-1} , NaHCO_3 1000 mg L^{-1} .

Figure 3.6 Inorganic carbon concentration in the receiver solution as a function of experimental time. Source solution: uranium concentration 1 mg L⁻¹, Na₂CO₃ 1000 mg L⁻¹.

Figure 3.7 Inorganic carbon concentration in the receiver solution as a function of experimental time. Source solution: uranium concentration 1 mg L⁻¹, NaHCO₃ 1000 mg L⁻¹.

3.3.5 Diffusion coefficient of uranium in humic acid model solutions

Humic substances are important complexing agents in natural waters and influence the overall diffusion rate coefficient of uranium considerably; therefore it is important to study the effect of humic substances on the diffusion of uranium. To determine the diffusion coefficients of uranium in humic acid solutions, two humic acid (HA) model solutions (10 mg L⁻¹ and 20 mg L⁻¹) were used. The overall diffusion coefficient of

uranium in humic acid model solutions was $4.9 \pm 0.8 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$ (Figure 3.8). This value is one order of magnitude lower than that in the model solutions without humic acid, indicating uranium forms complexes with humic acid, which has a big molecular size and molar mass. Therefore the diffusion of the large U-HA complex governs the overall diffusion coefficient of uranium in humic acid model solutions. Since the humic acid concentration is high in that model solution, the atmospheric CO_2 effect on the diffusion coefficient measurements is not significant (Appendix A). The diffusion coefficients of uranium in two humic acid concentrations are close, indicating the distribution of uranium species in the two model solutions were almost same. Similar effects of HA on the diffusion coefficient of other trace metal ions has been reported by other workers[17].

The diffusion coefficient of HA in two model solutions were also measured (Figures 3.9 and 3.10). HA might form a large molecule at high concentrations[18]. As shown in Figure 3.10, the rate of the HA flux to the receiver solutions in 20 mg L^{-1} HA concentration decreases with time, indicating that the gel pores might be blocked by accumulating the big molecules of HA. Wang et al. [19] have reported that in 8 mg L^{-1} HA, the diffusion coefficient of HA was $2.3\text{-}4.5 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$, which is close to our results in 10 mg L^{-1} HA model solutions ($3.9 \pm 0.7 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$).

Figure 3.8 Uranium concentration in receiver solution as function of experimental time. Source solution: uranium concentration 2 mg L⁻¹, HA 10 mg L⁻¹, pH 7.

Figure 3.9 Organic carbon concentration in receiver solution as function of experimental time. Source solution: uranium concentration 2 mg L⁻¹, HA 10 mg L⁻¹, pH 7.

Figure 3.10 Organic carbon concentration in receiver solution as function of experimental time. Source solution: uranium concentration 2 mg L⁻¹, HA 20 mg L⁻¹, pH 7.

3.3.6 Uranium species concentration on the surface of DGT binding layers

As shown in Figures 2.2 and 2.4, there are linear diffusion gradients of metal species in the diffusive gel layers, when the DGT system is in a steady-state. If we can determine the metal species concentration on the surface of DGT binding layers, we can easily

obtain the lability factor of metal species, α , which is used to evaluate the relative lability of metal species and will be discussed in Chapters 5 and 6.

Since it is very difficult to determine the concentration of a specific uranium species in between the diffusive layer and the binding layer, we measured the total uranium concentration in the diffusive layer instead. DGT devices were prepared following the procedures described in Chapter 2, using diffusive gel layers of 2 mm in thickness and 2.5 cm in diameter. Chelex-100 gel layers were used as binding layers. The DGT devices were then deployed in model solution containing uranium 1 mg L^{-1} only and model solutions containing uranium (1 mg L^{-1}) with complexing ligands: NaHCO_3 , fulvic acid (FA) and humic acid (HA), details shown in Figure 3.11. When the steady-state diffusion gradients formed (after few hours), the diffusive layers were removed from DGT devices immediately and eluted by 20% HNO_3 . The uranium in the elution was determined using ICP-MS. The volume of diffusive layer is 0.98 cm^3 and the total uranium concentrations in diffusive layer are 490, 578, 588 and $730 \text{ } \mu\text{g L}^{-1}$ for uranium only, U- NaHCO_3 , U-FA and U-HA model solutions, respectively.

If we assume the diffusion gradients in diffusive layers are linear, the total uranium concentrations we measured in the diffusive layer are equal to the median value of the uranium concentration in the concentration gradients, as shown in Figure 3.11. Since we know the total uranium concentration in bulk solution, we can draw a concentration gradient (Figure 3.11) and obtain the uranium concentration on the surface of DGT binding layers (intercept of linear curve). The uranium concentration on the surface of DGT binding layer is almost 0 for the model solution containing uranium only, indicating

the uranium species without complexing ligands are fully labile. The uranium concentrations on the surface of DGT binding layers for U- NaHCO_3 , U-FA and U-HA are 156, 177 and 461 $\mu\text{g L}^{-1}$, respectively. The U-HA is the most inert among these species.

Figure 3.11 Linear diffusion gradient in diffusive gel layers (2mm in thickness) in model solutions.

▲: uranium 1 mg L⁻¹, pH 7.

■: uranium 1 mg L⁻¹, NaHCO_3 0.001 mol L⁻¹, pH 8.

△: uranium 1 mg L⁻¹, fulvic acid 1 mg L⁻¹, pH 7.

◆: uranium 1 mg L⁻¹, humic acid 1 mg L⁻¹, pH 7.

3.4 References

1. Koryta, J.r., Dvorák, J.r., and Kavan, L. (1993). Principles of electrochemistry. In Principles of electrochemistry, 2nd Edition. (Chichester ; New York: Wiley), pp. 80-81.
2. Crank, J. (1956). The mathematics of diffusion (Oxford: Clarendon Press).
3. Li, Y.-H., and Gregory, S. (1974). Diffusion of ions in sea water and in deep-sea sediments. *Geochimica et Cosmochimica Acta* 38, 703-714.
4. Atkins, P.W. (1998). Physical chemistry. In Physical chemistry, 6th Edition. (New York: W.H. Freeman), p. 727.
5. Atkins, P.W. (1998). Physical chemistry, 6th Edition (New York: W.H. Freeman).
6. Atkins, P.W. (1982). Physical chemistry, 2nd Edition (New York: W.H. Freeman).
7. Zhang, H., and Davison, W. (1995). Performance Characteristics of Diffusion Gradients in Thin Films for the in Situ Measurement of Trace Metals in Aqueous Solution. *Analytical Chemistry* 67, 3391-3400.
8. Scally, S., Davison, W., and Zhang, H. (2003). In Situ Measurements of Dissociation Kinetics and Labilities of Metal Complexes in Solution Using DGT. *Environmental Science and Technology* 37, 1379-1384.
9. Zhang, H., and Davison, W. (1999). Diffusional characteristics of hydrogels used in DGT and DET techniques. *Analytica Chimica Acta* 398, 329-340.
10. Yezek, L.P., and Van Leeuwen, H.P. (2005). Donnan Effects in the Steady-State Diffusion of Metal Ions through Charged Thin Films. *Langmuir* 21, 10342-10347.
11. Fatin-Rouge, N., Milon, A., Buffle, J., Goulet, R.R., and Tessier, A. (2003). Diffusion and Partitioning of Solutes in Agarose Hydrogels: The Relative Influence of Electrostatic and Specific Interactions. *Journal of Physical Chemistry B* 107, 12126-12137.
12. Scally, S., Davison, W., and Zhang, H. (2006). Diffusion coefficients of metals and metal complexes in hydrogels used in diffusive gradients in thin films. *Anal. Chim. Acta* 558, 222-229.
13. Garmo, O.A., Royset, O., Steinnes, E., and Flaten, T.P. (2003). Performance Study of Diffusive Gradients in Thin Films for 55 Elements. *Analytical Chemistry* 75, 3573-3580.
14. Perry, D.L., Phillips, S.L., and Chung, J.D. (1988). Potentiostatic measurement of the diffusion coefficient of uranyl in carbonate media. *Inorganica Chimica Acta* 149, 301-304.
15. Kigoshi, K., and Hashitani, T. (1963). Self-diffusion coefficients of carbon dioxide, hydrogen carbonate ions, and carbonate ions in aqueous solutions. *Bulletin of the Chemical Society of Japan* 36, 1372.
16. Hashitani, T., and Kigoshi, K. (1965). Measurements of the self-diffusion coefficients of carbon dioxide, hydrogen carbonate ions, and carbonate ions in an aqueous medium. *Bulletin of the Chemical Society of Japan* 38, 1395-1396.
17. Scally, S., Davison, W., and Zhang, H. (2006). Diffusion coefficients of metals and metal complexes in hydrogels used in diffusive gradients in thin films. *Analytica Chimica Acta* 558, 222-229.
18. Shinozuka, N., and Lee, C. (1991). Aggregate formation of humic acids from marine sediments. *Marine Chemistry* 33, 229-241.

19. Wang, Y., Combe, C., and Clark, M.M. (2001). The effects of pH and calcium on the diffusion coefficient of humic acid. *Journal of Membrane Science* 183, 49-60.

Chapter 4

**Characterization of DGT binding
layers**

4.1 Introduction

DGT binding layers function as a metal sink, which can bind metal ions and lower the concentration of metal species on the surface of binding layer in order to form steady-state diffusive gradients in diffusive layer. As discussed in Chapter 2, the requirements for the DGT binding layer are:

- 1) Fast and irreversible binding with metal ions
- 2) Large capacity and is never saturated during the experiment
- 3) Stable in the natural water conditions

Several materials have been tested in this work and four of them have been chosen as the DGT binding layers: Chelex-100 ion-exchange resin, DE81 ion-exchange filter membrane, P81 ion-exchange filter membrane, and a new polymer, poly((salicylaldoxime-3,5-diyl (N,N'-dimethylethylenediamine N,N'-bismethylene))), polymer-A. In this chapter, the performance of the above four DGT binding layers is tested and discussed.

Chelex resins are styrene divinylbenzene copolymers containing paired iminodiacetate ions which act as chelating groups in binding polyvalent metal ions, as shown in Figure 4.1 . Chelex-100 resins have great selectivity and sensitivity to trace metal ions, and chelex-100 can work in a wide range of pH and ionic strength. Therefore Chelex-100 resin has been widely used in ion-exchange columns, trace metal removal [1, 2], metal analysis [3-5] and water testing in environmental and analytical laboratories. Imbedded

in polyacrylamide gel, Chelex-100 has been used as DGT binding layer since 1994 and has been considered as a traditional and standard DGT binding layer [6-9].

Figure 4.1 Change of the binding groups of Chelex-100 resins with increasing pH. (Biorad Chelex-100 Instruction Manual)

DE 81 is a basic anion exchanger with diethylaminoethyl functional groups. The ion exchange capacity is $1.7 \mu\text{eq}/\text{cm}^2$ when flow rate is 95 mm/30 min (Whatman). The amino-functional groups of DE 81 are immobilized on the neutral cellulose polymer, as shown in Figure 4.2. DE81 has been used in removal of metal ions[10]. Li et al. have used DE81 as DGT binding layer for the study of uranium speciation [8, 11] .

Figure 4.2 Function groups of DE-81 [11]

P81 is a thin (0.23 mm) cellulose phosphate paper (Figure 4.3), which is a strong cation exchanger of high capacity: ion exchange capacity is $18.0 \mu\text{eq}/\text{cm}^2$ when the flow rate is 125 mm/30 min (Whatman). P81 has been used in metal removal[10] and has been used as DGT binding layer for trace metals (e.g. copper) [12].

Figure 4.3 Function groups of cellulose phosphate.[10]

A new oxime containing polymer, poly (salicylaldoxime-3,5-diyl (N,N'-dimethylethylenediamine N,N'-bismethylene)), polymer-A, which has been used as chelating agent for trace metal ions by other workers[13], has been used in this work for the first time as DGT binding layer for the study of uranium speciation in aqueous media. The function groups of the polymer-A are shown in Figure 4.4.

These four DGT binding layers have been prepared and tested in model solutions to determine their performance characteristics for binding with uranium.

Figure 4.4 Function groups of polymer-A, (salicylaldoxime-3,5-diyl (N,N'-dimethylethylenediamine N,N'-bismethylene))[13]

4.2 Experimental

4.2.1 Reagents

Unless otherwise indicated, all chemicals used were of analytical grade. A 1000 mg L⁻¹ uranium standard solutions were purchased from SPEX Inc., US. Chelex-100 ion-

exchange resin of 200-400 mesh size was purchased from Bio-Rad Laboratories, US. Whatman DE 81 and P81 ion-exchange membrane of 2.5 cm diameter disc with 0.2mm thickness were purchased from Fisher Scientific Ltd. Canada. N,N'-dimethylethylenediamine were obtained from Sigma-Aldrich, Canada; Salicylaldehyde was obtained from Acros Organics, Belgium; formaldehyde solution (37%) was purchased from LabChem Inc., US; Dimethylformamide (DMF) was obtained from Caledon Laboratories Ltd., Canada. Chelex-100 resin gel was prepared as described in Chapter 2.

Concentrated Optima nitric acid (Fisher Scientific) was used for all acidic solution preparation unless otherwise stated. The acid and sodium hydroxide (Fisher Scientific) were used to adjust the solution pH.

4.2.2 Preparation of polymer-A DGT binding layers

As described earlier[13], polymer-A was prepared by dissolving 13.7 g of salicylaldehyde and 10.8mL of N,N'-dimethylethylenediamine in 180mL of DMF. To this solution, 19mL of 37% aqueous formaldehyde was slowly added with stirring at room temperature. After 4 hours, the mixture was heated, gradually in an oil bath, to 90°C and the heating was then continued for 4 more hours. An additional 10mL of 37% formaldehyde was slowly added to the reaction mixture in three portions. After 12 hours of continuous heating, the reaction mixture was cooled and the precipitate was collected and washed with methanol. After the soxhlet extraction with methanol for 24 hours, the polymer was dried in vacuum and crushed in a mortar. Satisfactory elemental analyses data were obtained using EA3000 Elemental Analyzer (EuroVector Instruments) and

found: %C 62.98, %H 7.30, and % N 13.94. The Calculation for $[C_{13}H_{19}N_3O_2]_n$ is: %C 62.63, %H 7.68, and % N 16.85.

0.3 g of polymer-A powder was added in 5 ml of the gel solution, which was prepared as described in Chapter 2. 30 μ l of ammonium persulphate solution and 12.5 μ l of TEMED were added into the above solution. The solution was well mixed and then pipetted immediately in between two glass plates, which was prepared as described in Chapter 2. The assembly was maintained at about 40°C for 1 hour until the gel was completely set and then the assembly was prised open. The polymer-A binding gel was then cut 2.5 cm in diameter.

4.2.3 Determination of uranium uptake by DGT binding layers

To test the performance of DGT binding layers, several model solutions were prepared by diluting uranium standard solution (1000 mg L⁻¹). To test the relationship between the uranium uptake and the time, the binding layers were examined by immersing the binding layers in 1000mL solutions containing 1.0 mg L⁻¹ uranium with a constant rate of stirring at pH 7 for several hours. To test the pH and ionic strength, the DGT binding layers were immersed into 100 μ g L⁻¹ uranium solutions at various pH and ionic strength for 24 hours. Then the uranium was eluted using 20% (v/v) HNO₃ and uranium concentration was determined using ICP-MS and KPA analyzer as described in Chapter 2. The performance test of DE81 was done by Weijia Li[14], who was a collaborator of our research group, at Radiation Protection Bureau, Health Canada.

4.3 Results and discussion

4.3.1 Effect of immersion time on uranium uptake by DGT binding layers

Effect of immersion time on uranium uptake by four DGT binding layers is presented in Figures 4.5 -4.8. The uranium uptake by the four DGT binding layers increases with time. A linear relationship between the uranium uptake and the experimental time has been found in the initial part of the curves. The adsorption of uranium by the DGT binding layers is surface reaction, which follows Langmuir isotherm equation[15], as follows:

$$K = k_a / k_{-a} \quad (4.2)$$

$$\theta = \frac{K[M]}{1 + K[M]} \quad (4.3)$$

$$v = k\theta = \frac{kK[M]}{1 + K[M]} \quad (4.4)$$

where M is metal ions, S is the binding sites, k_a is the rate coefficient for the forward reaction, k_{-a} is rate coefficient for the reverse reaction, and K is equilibrium constant for the adsorption process. θ is the fraction of the surface that is covered. The rate of reaction, v , is proportional to θ . If the concentration of M is high, the surface is well covered, $\theta \approx 1$, $v = k$, and the kinetics is zeroth order. If the concentration of M is low, $K[M] \approx 0$, the surface is sparsely covered, $v = k\theta = kK[M]$ and the kinetics is first-order.

The uranium concentration is considered unchanged and much higher than the binding sites on the DGT binding layers during the experiment since the surface area of DGT

binding layers is limited. Therefore, the kinetics of surface reaction is zeroth order. The rate coefficient is a constant, which is the slope of the curve of the uranium uptake versus the experimental time.

The uranium uptake rates are presented in Table 4.3. The rate of DE81 is higher than other binding layers, whereas the rate of P81 is the lowest. If we assume the concentration of uranium in the solution is $100 \mu\text{g L}^{-1}$, which is higher than that in unpolluted surface freshwaters (around $1 \mu\text{g L}^{-1}$), and the diffusion coefficient of uranium is $5 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$, which is the highest value of diffusion coefficient for uranium presented in Chapter 3, the diffusion rate of uranium that diffuses through a DGT diffusive layer is about $0.05 \text{ pmole cm}^{-2} \text{ s}^{-1}$. The diffusion rate of uranium is lower than the uranium uptake rates for the four DGT binding layers. Therefore the uranium can immediately bind with the DGT binding layers when diffusing through the diffusive layer and the uranium concentration on the surface of DGT binding layers can be considered as zero.

If the reaction time is long enough, all the binding layers should be saturated by uranium. The maximum capacity of DGT binding layers is presented in Table 4.3. Chelex-100, DE81 and polymer-A DGT binding layers have good binding capacity of uranium. P-81 has the lowest capacity among the four DGT binding layers. However, since in natural surface freshwaters the uranium concentration is very low, DGT binding layers are never saturated during the deployment time period.

Figure 4.5 The effect of immersion time on uranium uptake by the Chelex-100 DGT binding layer in uranium model solutions, pH 7. Initial concentration of uranium: 1.0 mg L⁻¹.

Figure 4.6 The effect of immersion time on uranium uptake by the DE 81 and the Chelex-100 DGT binding layers at pH 8.0, 23°C with initial uranium concentration of 1.0 mg L⁻¹ and NaHCO₃ concentration of 100 mg L⁻¹.
 ■: DE81; △: Chelex-100[14]

Figure 4.7 The effect of immersion time on uranium uptake by the P81 binding layers in 1 mg L⁻¹ uranium model solutions, pH 7.

Figure 4.8 The effect of immersion time on uranium uptake by the polymer-A DGT binding layer in 1 mg L⁻¹ uranium model solutions, pH 7.

4.3.2 Effect of pH on uranium uptake by DGT binding layers

pH influences both distribution of uranium species, as discussed in Chapter 3, and the function groups of the DGT binding layers. In the presence of atmospheric CO₂, the U-carbonate species and U-hydroxide species, which have negative charge, are the dominate species at high pH as discussed in Appendix A. The pH effect was presented in Figures 4.9 -4.12. Chelex 100 chelating resin is a styrene-divinylbenzene copolymer with imminodiacetate functional groups (Figure 4.1). At very low pH, the imine groups

and the carboxyl groups are protonated. The protonated nitrogen in imine groups has a positive charge, which can attract anions; whereas the carboxyl groups are neutral. As pH increases, carboxyl groups deprotonate and have negative charges; imine groups become neutral. Therefore anion sorption decreases and cation sorption increases with increasing pH. At $\text{pH} > 12$, the resin functions as a cation exchanger only[16]. However at low pH the predominant species of uranium are cationic forms and at high pH the predominant species of uranium are anionic forms, resulting in the low uranium uptake by Chelex-100 at very low and very high pH. The similar explanations can be applied to other binding layers. As an anion exchange filter paper, DE81 has a good binding capacity at the pH higher than 6; however when the pH is lower than 5, the capacity decreased significantly. For P81 and polymer-A binding layer, a wide optimum pH range for the uranium uptake has been observed. All of the four DGT binding layers have been found to be suitable for the applications in the range of natural freshwaters (pH 6-8). The large standard deviation of some samples probably results from the uneven distribution of binding sites in binding gel layers and the swelling effect.

Figure 4.9 Effect of pH on uranium uptake by the Chelex-100 DGT binding layer in $100 \mu\text{g L}^{-1}$ uranium model solutions, pH 2-9. Deployment time: 24 h.

Figure 4.10 Effect of pH on the uranium uptake of the DE 81 and the Chelex-100 DGT binding layers. Initial uranium concentration: 1.0 mg L⁻¹; deployment time: 24 h; temperature: 23°C.

■: DE81; △: Chelex-100[14]

Figure 4.11 Effect of pH on uranium uptake by the P81 DGT binding layer in $100 \mu\text{g L}^{-1}$ uranium model solutions, pH 3-11. Deployment time: 24 h.

Figure 4.12 Effect of pH on uranium uptake by the polymer-A DGT binding layer in 100 $\mu\text{g L}^{-1}$ uranium model solutions, pH 4-11. Deployment time: 24 h.

4.3.3 The effect of ionic strength on uranium uptake by DGT binding layers

The effect of ionic strength on the DGT binding layers are shown in Figures 4.13-4.16. Four DGT binding layers exhibited a similar trend. The uranium uptake by DGT binding layers decreased with increasing ionic strength, indicating the major ions in solutions affect the uranium binding on DGT binding layers. The major ions might compete with the uranium by binding with DGT binding layers and the activity coefficient of uranium

ion might decrease with increasing ionic strength at low ionic strength range ($< 0.5 \text{ mol L}^{-1}$). However, the binding capacity of uranium for the four DGT binding layers was adequate for the DGT applications in natural surface freshwaters even at high ionic strength, given the low uranium concentrations in freshwaters.

Figure 4.13 Effect of ionic strength on uranium uptake by the Chelex-100 DGT binding layer in $100 \mu\text{g L}^{-1}$ uranium model solutions, pH 7. NaNO_3 concentrations 0.0001 - 0.1 mol L^{-1} . Deployment time: 24 h.

Figure 4.14 Effect of ionic strength on uranium uptake by the DE 81 and the Chelex-100 DGT binding layers in solution of different NaNO₃ concentrations (M) at pH 8.0. Initial concentration of uranium: 1.0 mg L⁻¹; deployment time: 24 h; temperature: 23°C.

■: DE81; Δ: Chelex-100[14]

Figure 4.15 Effect of ionic strength on uranium uptake by the P81 binding layers in 100 $\mu\text{g L}^{-1}$ uranium model solutions, pH 7. NaNO_3 concentrations 0.0001-0.1 mol L^{-1} . Deployment time: 24 h.

Figure 4.16 Effect of ionic strength on uranium uptake by the polymer-A DGT binding layers in $100 \mu\text{g L}^{-1}$ uranium model solutions, pH 7. NaNO_3 concentrations $0.0001\text{-}0.1 \text{ mol L}^{-1}$. Deployment time: 24 h.

4.3.4 Swelling effect

Swelling effect, which affects not only the ease of the assembly of the DGT devices but also the accuracy of measurement[17], is an important property of gel based binding layer[18]. The degree of swelling effect of hydrogels usually depends on the pH and ionic strength [19]. Chelex-100 gel binding layer swells at low ionic strength and shrinks at high ionic strength. Some times, the Chelex-100 gel binding layers have to be conditioned in a solution with same ionic strength as the sample solutions before experiment. The swelling effect of polymer-A gel and the commercial ion-exchange filter (DE-81 and P81) is not significant.

4.3.5 DGT deployment in synthetic fresh water samples

To test the performance of binding layers in DGT experiment, DGT devices using Chelex-100, DE81 and polymer-A DGT as binding layers were deployed in synthetic fresh water, which had a similar condition as real surface freshwaters. The major inorganic ions, total organic and inorganic carbons in synthetic fresh water samples are shown in Table 4.1. DGT devices were assembled following the procedures described in Chapter 2. The uranium uptake by DGT increased with deployment time linearly (Figures 4.17 – 4.18), as expected, indicating the DGT binding layers were suitable for DGT *in-situ* applications. DE81 and polymer-A binding layers took more uranium than Chelex-100 in the same deployment period, indicating that DE81 and polymer-A might have high recoveries of uranium and might take more DGT-labile species. The DGT-labile species has been discussed in Chapter 5.

Table 4. 1 Major inorganic ions, total organic (TOC) and inorganic (TIC) carbons in synthetic fresh water samples

Synthetic fresh water sample (mg L ⁻¹)	
Ca ²⁺	35.2*
Mg ²⁺	8.9
Na ⁺	19
K ⁺	1.7
SO ₄ ²⁻	35.5
NO ₃ ⁻	2.8
Cl ⁻	62
HCO ₃ ⁻	50
Humic acid	1

*The synthetic fresh water sample was prepared from reagent grade chemicals. Standard deviation was not measured.

Figure 4.17 DGT mass–time curves for synthetic fresh water. ■: DE81; △: Chelex-100[14]. The dashed line is drawn based on theoretical calculation using DGT equation assuming all uranium species were measured.

Figure 4.18 DGT mass-time curves for synthetic fresh water.

●: Polymer-A DGT; ▲: Chelex-100 DGT.

4.3.6 Field studies in natural surface freshwaters

In order to test the DGT performance for *in-situ* analysis with different binding layers in natural freshwaters, we have done field deployment in the summer of 2005 and 2006, in St. Lawrence River. Chelex-100 and DE81 binding layers were used in 2005. DE81, Chelex-100 and polymer-A binding layers were used in 2006. The major inorganic ions, total organic and inorganic carbons in St. Lawrence River in 2006 are presented in Table 4.2. The results of the summer of 2005 show that the concentrations measured by DE 81 DGT and Chelex DGT were 73% and 60% of the total uranium, respectively[14]. In 2006,

the ratios of uranium concentrations measured by DE81 DGT and Chelex-100 DGT over total uranium concentration of St. Lawrence River ($0.35 \mu\text{g L}^{-1}$) were 98% and 49%[8], respectively. The results indicated a dependence of DGT measurements on the binding phases used in the devices. A long term field study done in 2007 will be discussed in Chapter 8.

Table 4.2 Major inorganic ions, total organic(TOC) and inorganic carbons (TIC) in St. Lawrence River in the summer of 2006

St. Lawrence River sample (mg L^{-1})	
Ca^{2+}	41.9 ± 0.3
Mg^{2+}	8.8 ± 0.8
Na^{+}	20.2 ± 0.3
K^{+}	2.5 ± 0.2
SO_4^{2-}	26.6 ± 0.2
NO_3^{-}	0.55 ± 0.03
Cl^{-}	33.7 ± 0.4
TOC	2.8 ± 0.5
TIC	19.9 ± 0.4

4.4 Conclusions

In this study, four chelating materials were used to be DGT binding layers and tested for uranium binding. Table 4.3 presents the overall assessment of the four DGT binding layers. The atmospheric CO₂ might affect the uranium speciation at pH > 6 and the uranium uptake by DGT binding layers. However all of the binding layers have enough capacity for the DGT experiment in natural fresh waters. Chelex-100, DE81 binding layers have good results at around neutral pH, whereas P81 and polymer-A binding layers works well at a wide pH range. With increasing ionic strength, the binding ability of all the binding layers decreases. When Chelex-100, DE81 and polymer-A binding layers were deployed in synthetic fresh water and in field studies, all of them showed good performance.

Table 4.3 Overall assessment of DGT binding layers

DGT binding layer	Uranium uptake rate ($\text{pmole cm}^{-2} \text{ s}^{-1}$)	Maximum capacity of uranium (nmole cm^{-2})	Swelling effect	Mechanical strength	Homogeneous distribution of functional groups	Assembly
Chelex-100	1.8	>80	Yes	good	not good	difficult
DE-81[14]	5.7	>200	No	very good	very good	very easy
P-81	0.9	>40	No	very good	very good	very easy
Polymer-A	1.9	>160	No	good	good	difficult

4.5 References

1. Davey, E.W., Gentile, J.H., Erickson, S.J., and Betzer, P. (1970). Removal of trace metals from marine culture media. *Limnology and Oceanography* 15, 486-488.
2. Jiann, K.-T., Wen, L.-S., and Santschi, P.H. (2005). Trace metal (Cd, Cu, Ni and Pb) partitioning, affinities and removal in the Danshuei River estuary, a macro-tidal, temporally anoxic estuary in Taiwan. *Marine Chemistry* 96, 293-313.
3. Chakraborty, P., Gopalapillai, Y., Murimboh, J., Fafous, I.I., and Chakrabarti, C.L. (2006). Kinetic speciation of nickel in mining and municipal effluents. *Analytical and Bioanalytical Chemistry* 386, 1803-1813.
4. Fafous, I.I., Yapici, T., Murimboh, J., Hassan, N.M., Chakrabarti, C.L., Back, M.H., Lean, D.R.S., and Gregoire, D.C. (2004). Kinetics of Trace Metal Competition in the Freshwater Environment: Some Fundamental Characteristics. *Environmental Science and Technology* 38, 4979-4986.
5. Hassan, N., Murimboh, J.D., and Chakrabarti, C.L. (2008). Kinetic Speciation of Ni(II) in Model Solutions and Freshwaters: Competition of Al(III) and Fe(III). *Water, Air, & Soil Pollution* 193, 131-146.
6. Zhang, H., and Davison, W. (1995). Performance Characteristics of Diffusion Gradients in Thin Films for the in Situ Measurement of Trace Metals in Aqueous Solution. *Analytical Chemistry* 67, 3391-3400.
7. Yapici, T., Fafous, I.I., Murimboh, J., and Chakrabarti, C.L. (2008). Investigation of DGT as a metal speciation technique for municipal wastes and aqueous mine effluents. *Analytica Chimica Acta* 622, 70-76.
8. Li, W., Li, C., Zhao, J., and Cornett, R.J. (2007). Diffusive gradients in thin films technique for uranium measurements in river water. *Analytica Chimica Acta* 592, 106-113.
9. Allaro-De Lu Torre, M.C., Beaulieu, P.Y., and Tessier, A. (2000). In situ measurement of trace metals in lakewater using the dialysis and DGT techniques. *Analytica Chimica Acta* 418, 53-68.
10. Kabay, N., Demircioglu, M., Yayli, S., Yuksel, M., Saglam, M., and Levison, P.R. (1999). Removal of metal ions from aqueous solution by cellulose ion exchangers. *Separation Science and Technology* 34, 41-51.
11. Tasdelen, C., Aktas, S., Acma, E., and Guvenilir, Y. (2009). Gold recovery from dilute gold solutions using DEAE-cellulose. *Hydrometallurgy* 96, 253-257.
12. Li, W., Zhao, H., Teasdale, P.R., John, R., and Zhang, S. (2002). Application of a cellulose phosphate ion exchange membrane as a binding phase in the diffusive gradients in thin films technique for measurement of trace metals. *Analytica Chimica Acta* 464, 331-339.
13. Ebraheem, K.A.K., Mubarak, M.S., and Al-Gharabli, S.I. (2002). Synthesis and chelation properties of some new mannich condensation polymers containing a salicylaldehyde group. *Journal of Macromolecular Science, Pure and Applied Chemistry* A39, 217-229.

14. Li, W., Zhao, J., Li, C., Kiser, S., and Cornett, R.J. (2006). Speciation measurements of uranium in alkaline waters using diffusive gradients in thin films technique. *Analytica Chimica Acta* 575, 274-280.
15. Laidler, K.J. (1987). Chemical kinetics. In *Chemical kinetics*, 3rd Edition. (New York: Harper & Row), pp. 229-245.
16. Ceo, R.N., Kazerouni, M.R., and Rengan, K. (1993). Sorption of silver ions by Chelex 100 chelating resin. *Journal of Radioanalytical and Nuclear Chemistry* 172, 43-48.
17. Warnken, K.W., Zhang, H., and Davison, W. (2004). Performance characteristics of suspended particulate reagent-iminodiacetate as a binding agent for diffusive gradients in thin films. *Analytica Chimica Acta* 508, 41-51.
18. Brazel, C.S., and Peppas, N.A. (1995). Synthesis and Characterization of Thermo- and Chemomechanically Responsive Poly(N-isopropylacrylamide-co-methacrylic acid) Hydrogels. *Macromolecules* 28, 8016-8020.
19. Durmaz, S., and Okay, O. (2000). Phase separation during the formation of poly(acrylamide) hydrogels. *Polymer* 41, 5729-5735.

Chapter 5

**DGT-labile uranium species in aquatic
systems**

5.1 Introduction

It is very easy to interpret data and explain the DGT results in model solutions because all the speciation parameters (diffusion coefficients, uranium concentrations, ionic strength, HS concentrations and other factors) are well known. However when DGT is deployed in real surface freshwaters, many problems have been found. All the speciation parameters are unknown in the natural freshwaters during the experiment because they may vary with time. Even the overall diffusion coefficient is unknown because the distribution of the uranium species in real freshwater samples is unknown. Those are the challenges that all the DGT researchers have to face.

The uranium accumulated on the DGT binding layers is the integration of the flux of all available uranium species, so-called DGT-labile species, during the experimental period. The objective of the study in this chapter is to present a theory that connects the link between the uranium uptake by DGT and uranium speciation in aqueous samples. The concepts of 'effective uranium concentration' and 'lability factor' have been used to interpret the DGT results avoiding interference from the variations of diffusion coefficients of uranium and other speciation parameters in aqueous media.

5.1.1 DGT-labile species

Since DGT is an indirect speciation tools, and cannot separate or determine a specific species in aquatic systems, what DGT really measures is the contribution of all species. In natural waters, metal species includes free metal ions and metal ligand complexes. The total mass of metal (M_{total}) consists of the following:

$$M_{total} = \sum_i M_i = M_{free} + ML_1 + ML_2 + \dots + ML_n \quad (5.1)$$

where M_i is the metal species, $ML_1, ML_2 \dots ML_n$ represent different metal ligand complexes in natural waters. If we assume all the species are fully labile and the binding layer is an ideal binding layer, which is never saturated, the concentration of all the metal species on the surface of the binding layer is zero. According to the mass balance and Eq. 5.1, the total metal accumulated by the binding layer (M_{DGT}) is equal to the total metal that diffuses through the diffusive layer (M_{diff}):

$$M_{DGT} = M_{diff} = \sum_i \frac{tA}{\Delta g} D_{M_i} c_{M_i} = \frac{tA}{\Delta g} (D_{M_{free}} c_{M_{free}} + D_{ML} c_{ML} + \dots + D_{ML_n} c_{ML_n}) \quad (5.2)$$

where D_{M_i} is the diffusion coefficient of M_i , c_{M_i} is concentration of M_i , Δg is the thickness of the diffusive layer, A is the area of the window of DGT device and t is the experimental time. Since not all the species are fully labile in the DGT experiment, the concentration of metal species on the surface of the binding layer is not always zero. When a steady-state diffusion gradient is established, the mass of metal accumulated in the binding layer is:

$$M_{DGT} = \sum_i \frac{tA}{\Delta g} D_{M_i} (c_{M_i} - c'_{M_i}) = \frac{tA}{\Delta g} [D_{M_{free}} (c_{M_{free}} - c'_{M_{free}}) + D_{ML_1} (c_{ML_1} - c'_{ML_1}) + \dots + D_{ML_n} (c_{ML_n} - c'_{ML_n})] \quad (5.3)$$

where c'_{M_i} is the concentration of M_i on the surface of the binding layer.

We define the lability factor, α_i , as:

$$\alpha_i = \frac{c_{M_i} - c'_{M_i}}{c_{M_i}} \quad (5.4)$$

The Eq. 5.3 can then be simplified as:

$$M_{DGT} = \sum_i \frac{tA}{\Delta g} D_{M_i} \alpha_{M_i} c_{M_i} = \frac{tA}{\Delta g} [D_{M_{free}} \alpha_{M_{free}} c_{M_{free}} + D_{ML_1} \alpha_{ML_1} c_{ML_1} + \dots + D_{ML_n} \alpha_{ML_n} c_{ML_n}] \quad (5.5)$$

If $c'_{M_i} = 0$, $\alpha_i = 1$, the metal species is totally labile; if $c'_{M_i} = c_{M_i}$, $\alpha_i = 0$, the metal species is totally inert; if $0 < c'_{M_i} < c_{M_i}$, $0 < \alpha_i < 1$, the metal species is partially labile.

5.1.2 Effective uranium concentration

According to Eq. 5.5, the uranium accumulated (M_U) by the binding layer is:

$$M_U = \sum_i \frac{tA}{\Delta g} D_{U_i} \alpha_{U_i} c_{U_i} \quad (5.6)$$

However, since uranium speciation in aqueous media is complex, it is difficult to obtain D_{U_i} and α_{U_i} of all the uranium species. To overcome this problem, the overall diffusion coefficient D_U of uranium and the overall lability factor α_U in a reference uranium model solution (pH 7, temperature 25°C, containing 0.01 mol L⁻¹ NaNO₃, no complexing ligand) are used for all the species. The α_U is 1, since uranium species in that condition is considered as totally labile. The effective uranium concentration c_{Ueff} is defined and used to interpret the experimental data by Eq. 5.7.

$$M_U = \frac{tA}{\Delta g} D_U \alpha_U c_{U_{eff}} = \frac{tA}{\Delta g} D_U c_{U_{eff}} \quad (5.7)$$

$$c_{U_{eff}} = \frac{M_U \Delta g}{tA D_U} \quad (5.8)$$

$c_{U_{eff}}$ of an unknown sample is the equivalent uranium concentration in the reference condition of pH 7, 25°C, and no complexing ligand, in which the DGT device can accumulate the same amount of uranium during the same deployment time as in the unknown sample. Warnken et al. [1] have also defined the effective concentration as C_{DGT} , which is the sum of the contributions of the different complexes via diffusion. If the same diffusion coefficient, D_U , is used, the value of $c_{U_{eff}}$ is equal to that of C_{DGT} .

$c_{U_{eff}}$ also reflects the contributions of all species. Comparison of Eq. 5.6 and Eq. 5.7, gives:

$$\frac{tA}{\Delta g} D_U \alpha_U c_{U_{eff}} = \sum_i \frac{tA}{\Delta g} D_{U_i} \alpha_{U_i} c_{U_i} \quad (5.9)$$

$$c_{U_{eff}} = \sum_i \frac{D_{U_i} \alpha_{U_i}}{D_U \alpha_U} c_{U_i} \quad (5.10)$$

We define the apparent lability factor, ϕ_{U_i} , as

$$\phi_{U_i} = \frac{D_{U_i} \alpha_{U_i}}{D_U \alpha_U} \quad (5.11)$$

Eq. 5.10 can be simplified as:

$$c_{U_{eff}} = \sum_i \phi_{U_i} c_{U_i} \quad (5.12)$$

$\phi_{U_i} c_{U_i}$ reflects the contribution of the uranium species U_i to the effective uranium concentration $c_{U_{eff}}$.

The apparent lability factor and effective uranium concentration depends on both mobility (diffusion) and lability of uranium species. The proportion of the effective uranium concentration $c_{U_{eff}}$ to the total uranium concentration $c_{U_{total}}$ is defined as the percentage of DGT-labile uranium species (%L)

$$\%L = \frac{c_{U_{eff}}}{c_{U_{total}}} \times 100\% = \frac{\sum_i \phi_{U_i} c_{U_i}}{c_{U_{total}}} \times 100\% = \sum_i \phi_{U_i} \frac{c_{U_i}}{c_{U_{total}}} \times 100\% \quad (5.13)$$

We define the percentage distribution of the uranium species, θ_{U_i} , as

$$\theta_{U_i} = \frac{c_{U_i}}{c_{U_{total}}} \times 100\% \quad (5.14)$$

Eq. 5.13 can be simplified as:

$$\%L = \sum_i \phi_{U_i} \theta_{U_i} \quad (5.15)$$

The objective of this Chapter is to study the effects of speciation parameters on %L, $c_{U_{eff}}$, ϕ_{U_i} and θ_{U_i} . By now, it is impossible to differentiate between the effect of mobility (diffusion) and the effect of lability factor because the metal uptake on DGT binding layers reflects both the contribution of diffusion and binding kinetics of the metal species.

In Chapter 6, competitive ligand exchange method (CLEM) is used to determine the lability factor, α , of uranium species.

5.1.3 Humic substance as metal-binders

The binding sites of HS can be classified as major and minor types [2]. The major sites such as carboxylate groups, phenolate groups, dicarboxylic acid group and salicylic acid group, comprise ~90-99% of the binding sites and are weak binders of trace metal ions. The metal ions bind with weak binding sites, resulting in formation of weak complexes, which are labile and readily dissociate in aqueous media. HS also possess minor sites (e.g. S-, P-, and N-containing ligands) [3], which comprise ~1-10% of the binding sites[4], and are strong binders of metal ions, form strong complexes which do not dissociate. According to the requirements of thermodynamics, metal ions at extremely low concentrations, such as present in pristine waters (uncontaminated by metals), first bind with the strongest available binding sites, forming strong complexes which do not dissociate. After the metal ions have bound all the strong binding sites of HS, saturating them completely, the remaining metal ions then bind with the weaker binding sites, resulting in weak complexes, which are labile.

A trace metal, such a copper, which is ubiquitous in natural waters, is known to occupy the binding sites of HS. Hence, this work has included a study of the competition of copper with the analyte metal uranium for the binding of HS.

5.2 Experimental

5.2.1 Reagents

All sample solutions were prepared with deionized water of resistivity of 18.2 M Ω -cm, obtained direct from a NANOpure Diamond Ultrapure Water System (Barnstead, USA). All reagents used for the preparation of polyacrylamide gel and Chelex-100 gel were of analytical grade. The acrylamide monomer solution (40%) and Chelex 100 resin of 200–400 mesh were obtained from Bio-Rad. Ammonium persulphate and N,N,N',N'-tetramethylethylenediamine were obtained from Fisher Scientific, Inc., Canada. Agarose derived crosslinker (2%) and the DGT holders were purchased from DGT Research Ltd. UK. Cellulose nitrate filter membrane (0.45 μ m) was purchased from Fisher Scientific, Canada. 1000 mg L⁻¹ uranium and copper standard solutions were purchased from SPEX Inc., USA. Concentrated Optima nitric acid (Fisher Scientific) was used for preparation of all acidic solutions. All experiments were carried out in high-density polypropylene vessels.

A stock solution of 1.0 g L⁻¹ HA was prepared by dissolving approximately 1.0 g HA, which had been supplied by Dr. Les Evans (University of Guelph, Guelph, Ontario, Canada), in sodium hydroxide. The solution was made up to 1 L and stored in the dark at 4°C. A stock solution of 1.0 g L⁻¹ FA was prepared using Suwannee River Fulvic Acid, obtained from International Humic Substances Society (IHSS).

5.2.2 The preparation of DGT diffusive layers and binding layers

Polyacryamide gel has been used as diffusive layers and Chelex-100 resin gel layers have been used as binding layers. The preparation of DGT diffusive layers and binding layers followed the procedures described in Chapter 2.

5.2.3 Model solutions

A series of model solutions were prepared by adding known amounts of the HA or FA stock solution to 2L uranium solutions ($100 \mu\text{g L}^{-1}$). The HA in these solutions were 0.1 to 20 mg L^{-1} , which was set within the range of freshwater conditions; the FA concentrations in the FA model solutions were 0.1 to 10 mg L^{-1} . To investigate competition between copper and uranium, the copper standard solution was added to the series of model solutions to make the individual member of the above series contain copper concentrations of 0, 50, 100 and $150 \mu\text{g L}^{-1}$. The pH of all model solutions was adjusted to 7, and the pH was re-checked and re-set at 7 just prior to use if there was and drift in the set pH 7 in the intervening period. The distribution of uranium species in model solutions was calculated using the Visual MINTEQ program.

5.2.4 DGT deployment

The Chelex-100 binding layer, the polyacryamide diffusion layer and cellulose nitrate filter membrane were placed in a DGT holder according to the previously described procedure[5] in Chapter 2. The DGT holders were deployed in Teflon containers (2.2 L) containing 2L of model solutions. These containers were placed in a Water-Bath Shaker (Model C76 Water-Bath Shaker, New Brunswick Scientific, USA) and the temperature

was set at 25°C. The DGT holders were removed from the solutions after deployment for 5-72 hours. The binding layers were taken from DGT holders and the bound metals eluted in 2.0 mL of 20% (v/v) HNO₃ solution, reacting for 24 hours; the uranium concentration in the eluted solution was quantitatively determined using KPA.

5.2.5 Determination of uranium

A Kinetic Phosphorescence Analyzer, KPA-10 (ChemChek Instruments, Inc.), was used to determine uranium concentration. 1.5 mL UraplexTM (ChemChek Instruments, Inc) solution was added to each sample to enhance the uranyl phosphorescence.

5.3 Results and discussion

5.3.1 Overall diffusion coefficient D_U and overall lability factor α_U in reference model solution

The overall diffusion coefficient of uranium D_U , was determined (Chapter 3) according to the method previously described[6, 7]. The source and receptor solutions contained 0.01 mol L⁻¹ NaNO₃ and the pH was adjusted to 7. The temperature during the experiment was 25°C. The value of D_U was $1.5 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ in the diffusive gel. D_U is an overall diffusion coefficient, which is a weighted average of the diffusion coefficients of all uranium species; the weighting factor is the percentage of each individual uranium species.

One assumption of this investigation is that in the reference model solution the overall lability factor α_U was taken to be 1, which means that all the uranium species in this condition are assumed to be fully labile. In the preliminary study, the percentage of DGT-

labile uranium species, %L, calculated using Eq. 5.15, in the uranium model solution of $100 \mu\text{g L}^{-1}$ uranium plus 0.01 mol L^{-1} NaNO_3 at pH 7 (reference model solution) was found to be above 90%, which validated the above assumption.

To investigate the impact of atmospheric CO_2 on the reference model solutions, another experiment has been done. Chelex-100 DGT devices were deployed in the reference model solution, which was bubbled with nitrogen gas (N_2) to expel air. The percentage DGT-labile species %L was about 95% in that experiment (Appendix A). The uranium species in the reference model solutions could be considered as fully labile, whether or not they were bubbled with nitrogen. Therefore the presence or absence of atmospheric CO_2 did not change uranium uptake by DGT in reference model solutions.

5.3.2 Effective uranium concentration in humic acid and fulvic acid model solutions

Humic substances (HS) consists of fulvic acid, humic acid, and humin, which represent typically 40%-99% of Dissolved Organic Carbon(DOC)[8, 9]. Fulvic acid and humic acid are important complexing agents for uranium in natural waters at neutral or low pH.

Figures 5.1 and 5.2 present the percentage of DGT-labile uranium species (%L) in humic acid and fulvic acid model solutions, respectively. The total uranium concentration was $100 \mu\text{g L}^{-1}$ in each model solutions and the predominant species were U-HA or U-FA species. The effective uranium concentration decreased with increasing humic acid and fulvic acid concentration, which indicated the binding of uranium with HA and FA

decreased the lability of uranium species. Similar results were found for other metal ions by Li et al.[10], who reported that the DGT-labile fractions of copper and cadmium decreased in presence of humic acid.

If we assume there is only one U-HA species in the model solutions, the percentage distribution of uranium species, θ_{U-HA} is 100%. Therefore the percentage of DGT-labile uranium species, %L, is equal to the apparent lability factor, ϕ_{U-HA} . According to Eq. 5.11, $\%L = \phi_{U-HA} = \frac{D_{U-HA}\alpha_{U-HA}}{D_U\alpha_U}$, and the lability factor, $\alpha_{U-HA} = \frac{\%L \times D_U \times \alpha_U}{D_{U-HA}}$. However, the binding sites of HS can be classified as major and minor types [2]. The minor binding sites are stronger than the major binding sites, however, they are in small proportion[4]. Metal ions first bind the minor (strong) binding sites, and then, bind the major (weak) binding sites. With increasing concentrations of HS, a greater proportion of uranium binds to strong binding sites of HS, resulting in decreasing lability factor α_{U-HS} and apparent lability factor ϕ_{U-HS} of U-HS complex.

If we assume there are two uranium species (strong and weak) in U-HA model solutions. Eq. 5.15 can be rewritten as:

$$\%L = \phi_{Us}\theta_{Us} + \phi_{Uw}\theta_{Uw} \quad (5.16)$$

where ϕ_{Us} and θ_{Us} are the apparent lability factor and the percentage distribution of the uranium binding with strong binding sites of humic acid, ϕ_{Uw} and θ_{Uw} are those with weak binding sites of humic acid. The constraint for Eq. 5.16 is:

$$\theta_{Us} + \theta_{Uw} = 1 \quad (5.17)$$

Figure 5.1 Percentage of DGT-labile uranium species (%) as a function of the HA concentration, in uranium-HA model solutions. Uranium concentration $100 \mu\text{g L}^{-1}$, HA concentration: 0.1, 0.5, 1, 2, 3, 4 and 5 mg L^{-1} .
 ◆: Cu $0 \mu\text{g L}^{-1}$. ▲: Cu $50 \mu\text{g L}^{-1}$. ■: Cu $100 \mu\text{g L}^{-1}$.

Figure 5.2 Percentage of DGT-labile uranium species (%) as a function of the FA concentration, in uranium-FA model solutions. Uranium concentration $100 \mu\text{g L}^{-1}$, NaNO_3 0.01 mol L^{-1} , FA concentration: 0.1, 0.5, 1, 2, 5 and 10 mg L^{-1} . $\blacklozenge$: Cu $0 \mu\text{g L}^{-1}$ $\blacktriangle$: Cu $50 \mu\text{g L}^{-1}$ $\blacksquare$: Cu $100 \mu\text{g L}^{-1}$.

The molar mass of HA was estimated according to its bidentate complexing capacity of HA of 4.88 mmol g^{-1} [11]. In the U-HA model solutions, when the HA concentration was 0.1 mg L^{-1} , U/HA molar ratio was about 0.86, and almost all uranium ($>99\%$) was considered to bind to the weak binding sites. Therefore θ_{Uw} was considered as 1, and ϕ_{Uw} was equal to %L (96.1%). When the HA concentration was higher than 10 mg L^{-1} , U/HA molar ratio was lower than 0.01 and most of uranium bound to the strong binding sites.

θ_{Us} was considered as 1, and ϕ_{Us} was the value of %L (0.6%). Since ϕ_{Uw} and ϕ_{Us} were known, the percentage distribution θ_{Uw} and θ_{Us} could be calculated using Eq. 5.16 and Eq. 5.17 for other HA concentrations, as shown in Table 5.1. The uranium binding with strong binding sites increased with increasing HA concentration as expected. Two points should be noted: 1) Since the binding sites of HS have continuous distributions [12, 13], the classification of strong and weak binding sites may not be enough to clarify the uranium binding with HS. 2) At low U/HS ratios, the inorganic species of uranium cannot be ignored. In these data fitting, the inorganic species of uranium cannot be differentiated from the uranium binding with weak binding sites of HS. Even though the results are rough, they can provide some valuable information about uranium speciation in HS solutions.

Comparison of Figure 5.1 and 5.2 shows that when the concentration of HA and FA was equal, the percentage of DGT-labile uranium species in humic acid model solutions was lower than that in fulvic acid, indicating U-FA species are more labile than U-HA species, since the diffusion coefficient of HA and FA are quite similar [14, 15]. Our results agreed with those of Lenhart et al. [16], who reported that the binding of U(VI) by humic acid (HA) was stronger than that by fulvic acid and exhibited a larger pH dependence.

Table 5.1 Percentage distribution of uranium species in the HA model solutions. Uranium concentration $100 \mu\text{g L}^{-1}$, HA concentration: $0.1\text{-}20 \text{ mg L}^{-1}$, Cu $50, 100 \mu\text{g L}^{-1}$, pH 7. θ_{Uw} represents the percentage of uranium binding with weak binding sites, whereas θ_{Us} represents the percentage of uranium binding with strong binding sites.

HA concentration (mg L^{-1})	Percentage of uranium species (%) [*]					
	$\text{U } 100 \mu\text{g L}^{-1}$		$\text{U } 100 \mu\text{g L}^{-1}, \text{Cu } 50 \mu\text{g L}^{-1}$		$\text{U } 100 \mu\text{g L}^{-1}, \text{Cu } 100 \mu\text{g L}^{-1}$	
	$\theta_{Uw} (\%)$	$\theta_{Us} (\%)$	$\theta_{Uw} (\%)$	$\theta_{Us} (\%)$	$\theta_{Uw} (\%)$	$\theta_{Us} (\%)$
0.1	100.0	0.0	86.7	13.3	97.6	2.4
0.5	7.0	93.0	23.4	76.6	46.6	53.4
1.0	7.4	92.6	18.8	81.2	36.4	63.6
2.0	1.5	98.5	4.4	95.6	9.6	90.4
3.0	0.8	99.2	1.9	98.1	3.8	96.2
4.0	0.0	100.0	0.8	99.2	2.1	97.9
5.0	0.0	100.0	0.4	99.6	1.6	98.4
10.0	0.0	100.0	0.0	100.0	0.5	99.5
12.5	0.0	100.0	0.0	100.0	0.0	100.0
15.0	0.0	100.0	0.0	100.0	0.0	100.0
20.0	0.0	100.0	0.0	100.0	0.0	100.0

^{*} These values were theoretically calculated by data fitting and the standard deviation was not calculated.

Atmospheric CO_2 might affect the uranium uptake by DGT, when the HA concentration is less than 0.6 mg L^{-1} or the FA concentration is less than 1 mg L^{-1} as discussed in Appendix A. The inorganic U-carbonate species could be considered as labile species, which cannot be differentiated from the uranium binding with weak binding sites of HA or FA.

5.3.3 Competition of copper and uranium in model solutions

When copper was spiked into U-HA and U-FA model solutions, the effective uranium concentration and the percentage of DGT-labile uranium species increased with increasing copper concentrations, which can be attributed to the competition of copper with uranium for binding with humic acid or fulvic acid (Figures 5.1 and 5.2). In U-HA model solutions, θ_{Uw} values increased with a corresponding decreasing in the θ_{Us} values, as the copper concentration was increased from 0 to 100 $\mu\text{g L}^{-1}$ at the same HA concentration level (Table 5.1). The effect of the competition of copper was more significant in the HA concentration range of 0.5-2 mg L^{-1} , in which the strong binding sites were not in excess of all the metal ions (both uranium and copper). The uranium bound to the strong binding sites of the HA was replaced by copper because of the stronger affinity of copper for binding with HA[17]. The competition between uranium and copper also occurs for the weak binding sites of the HA if all the strong binding sites of the HA have been occupied by copper.

There is no significant competition between copper and uranium at low and high HA concentration because at low HA concentrations ($< 0.5 \text{ mg L}^{-1}$) a large part of uranium species are inorganic species, which are fully labile; whereas at high HA concentrations ($> 2 \text{ mg L}^{-1}$), the strong binding sites are in large excess of all the metal ions (uranium and copper) and no competition occurs. The significant range for FA is wider, from 0.1 mg L^{-1} to above 5 mg L^{-1} , indicating that the strong binding sites in FA are less than that in HA.

5.3.4 Ionic strength effect

The ionic strength in natural waters ranges from below 0.01 mol L^{-1} (inland water) to 0.7 mol L^{-1} (seawater) [18]. The effect of ionic strength on DGT is complex. First, at low ionic strength (less than 0.1 mmol L^{-1}), the diffusion coefficient of metal ions is 50% lower because of the Donnan potential in the charged gel[19]. Lower diffusion coefficient results in less metal mass being accumulated in DGT binding layer and less effective uranium concentration. Secondly, since the major cations, such as calcium and magnesium, act as competitors to trace metal ions, the metal binding efficiency of Chelex-100 binding layer is reduced at high salt concentrations[20]. Finally, increasing ionic strength gives rise to a greater concentration of free metal ions in humic acid and fulvic acid model solutions because the ionic atmosphere (ionic strength) profoundly affects electrostatic interactions between metal ions and humic substances[17]. Figure 5.3 presents the percentage of DGT-labile uranium species in the HA model solutions containing $0.01 \text{ mol L}^{-1} \text{ NaNO}_3$. The effective uranium concentration in the HA model solutions with NaNO_3 is higher than those without NaNO_3 (Figure 5.1), which indicates the overall effect of increasing ionic strength is to increase the effective uranium concentrations in uranium-HA model solutions. Copper also competes with uranium in the U-HA model solutions containing $0.01 \text{ mol L}^{-1} \text{ NaNO}_3$. The difference of effective uranium concentration between the different copper concentration levels in the U-HA model solutions containing $0.01 \text{ mol L}^{-1} \text{ NaNO}_3$ is not as significant as that in the U-HA model solutions containing no NaNO_3 .

5.3.5 The pH effect on uranium DGT-labile species in U-HA model solutions

Figure 5.4 presents the pH effect on the percentage of DGT-labile uranium species in the U-HA model solutions. The pH ranged from 5 to 10, which covered the pH range in natural waters. At pH 5, 6 and 7, the percentage of DGT-labile uranium species were at very low levels, indicating that the uranium binding with HA was strong enough to resist the protonation at those pHs. However, at higher pHs, the percentage of DGT-labile uranium species increased considerably, probably because of the formation of the U-OH species, which may be more labile than U-HA species and have greater diffusion coefficients. There is no significant atmospheric CO₂ impact on this experiment because the U-carbonate species is less than 0.1% of total uranium if the CO₃²⁻ concentration in the above model solutions is 1 mg L⁻¹, as discussed in Appendix A.

U-HA and U-OH species, such as UO₂(OH)₃⁻ and UO₂(OH)₂, are the major species in the above model solutions (Table 5.2). According to Eq. 15, the percentage of DGT-labile uranium species in the above model solutions can be calculated by summing the contributions of the two major species.

$$\%L = \varphi_{U-HA} \theta_{U-HA} + \varphi_{U-OH} \theta_{U-OH} \quad (5.18)$$

where φ and θ represent the apparent lability factors and the percentage distributions of the major species, U-HA and U-OH.

Figure 5.3 Percentage of DGT-labile uranium species (%) as a function of HA concentration, in uranium-HA model solutions. Uranium concentration $100 \mu\text{g L}^{-1}$, NaNO_3 0.01 mol L^{-1} , HA concentration: 0.1, 0.5, 1, 2, 5 and 10 mg L^{-1} . $\blacklozenge$: Cu $0 \mu\text{g L}^{-1}$ $\blacktriangle$: Cu $50 \mu\text{g L}^{-1}$ $\blacksquare$: Cu $100 \mu\text{g L}^{-1}$ $\times$: Cu $150 \mu\text{g L}^{-1}$.

Figure 5.4 Percentage of DGT-labile uranium species (%) as a function of pH, in uranium-HA model solutions. Uranium concentration $100 \mu\text{g L}^{-1}$, HA concentration 2 mg L^{-1} , NaNO_3 0.001 mol L^{-1} ,

The distributions of uranium species in the model solution (Table 5.2) and the percentage of DGT-labile uranium species %*L* were fitted to Eq. 5.18 using multiple linear regression. As discussed before, the U-HA consisted of different species with different binding site types, however, all the U-HA species were considered as one species (U-HA) to simplify the data fitting. The apparent lability factor ϕ , which were obtained from the data fitting, for U-HA and U-OH were 0.04 and 0.26, respectively (Table 5.2). ϕ_{U-HA} reflects the overall apparent lability factor of all types of binding sites of HA. The results indicated U-OH, which had higher ϕ value, might be more “labile” than U-HA species for DGT experiment. As discussed in Chapter 3, the diffusion coefficients of small U-OH species are greater than that of U-HA species. The greater apparent lability factor of U-OH might result from both the higher lability factor and greater diffusion coefficient. In freshwater, the typical pH is around 7. Slightly enhanced pH may cause significant increase in the uranium DGT-labile species.

5.3.6 Effect of carbonate ion on uranium DGT-labile species in U-HA model solutions

Carbonate is a very important complexing agent for uranium. U-Carbonate and U-OH-Carbonate species are predominant uranium species at high pH value in natural waters. Figure 5.5 presents the effect of carbonate ions on uranium DGT-labile species in presence of humic acid (2 mg L⁻¹). The pH of model solutions was around 8, and the ionic strength of model solutions was about 0.01 mol L⁻¹. NaHCO₃ concentrations ranged from 0.1 to 10 mmol L⁻¹. The DGT-labile uranium species increased with increasing

NaHCO₃ concentration from 0.1 to 2 mmol L⁻¹; however, it decreased with increasing NaHCO₃ concentration when the NaHCO₃ concentration was higher than 2 mmol L⁻¹.

Table 5.2 Percentage distribution of uranium species (%) in uranium-HA model solutions, calculated using Visual MINTEQ program. Uranium concentration was 100 µg L⁻¹, HA concentration 2 mg L⁻¹, NaNO₃ 0.001 mol L⁻¹, pH: 5, 6, 7, 8, 9, and 10. ϕ represents the apparent lability factor of the uranium species in those model solutions. Assuming CO₃²⁻ concentration is 1 mg L⁻¹.

pH	Percentage of uranium species (%) [*]	
	U-HA	U-OH
5	98.9	0.0
6	99.3	0.0
7	98.2	0.0
8	80.1	17.5
9	28.6	70.6
10	6.5	92.7
ϕ	0.04	0.26

^{*}These values were theoretically calculated by data fitting and the standard deviation was not calculated.

Figure 5.5 Percentage of DGT-labile uranium species (%) as a function of concentration of NaHCO₃, in uranium-HA model solutions. Uranium concentration 100 µg L⁻¹, HA concentration 2 mg L⁻¹, NaNO₃ 0.01 mol L⁻¹, concentration of NaHCO₃ 0.1, 0.5, 1, 2, 5 and 10 mmol L⁻¹.

There are three major uranium species in these model solutions, U-HA, UO₂(CO₃)₃⁴⁻ and UO₂(CO₃)₂²⁻. Therefore, Eq. 15 can be rewritten as Eq. 5.19. The percentage of U-HA decreased with increasing NaHCO₃ concentration, whereas that of UO₂(CO₃)₃⁴⁻ increased with the increasing NaHCO₃ concentration. The percentage distribution of UO₂(CO₃)₂²⁻

(Figure 5.6) showed a trend similar to that of the DGT-labile uranium species in these model solutions (Table 5.3).

$$\%L = \varphi_{U-HA} \theta_{U-HA} + \varphi_{UO_2(CO_3)_3^{4-}} \theta_{UO_2(CO_3)_3^{4-}} + \varphi_{UO_2(CO_3)_2^{2-}} \theta_{UO_2(CO_3)_2^{2-}} \quad (5.19)$$

The percentage distribution data of the three major species were also fitted to Eq. 5.19 using multiple linear regression. The apparent lability factor φ for U-HA, $UO_2(CO_3)_2^{2-}$ and $UO_2(CO_3)_3^{4-}$ were 0.62, 3.21 and 0.19, respectively (Table 5.3). The results indicated $UO_2(CO_3)_2^{2-}$, which had a higher φ value, might be more “labile” than the other two major uranium species, and probably played an important role in the uranium speciation in the above model solutions. The apparent lability factor of $UO_2(CO_3)_2^{2-}$ is higher than 1, which meant it is more ‘labile’ than the uranium species in the reference solution without any complexant, probably because the diffusion coefficient of $UO_2(CO_3)_2^{2-}$ is higher than the overall diffusion coefficient of uranium in the reference model solutions.

The previously published work on the uranium speciation in St. Lawrence River using DGT technique[7] reported that the DGT-labile fraction was about 73% for DE81 anion-exchange filter as the binding layer and 60% for Chelex-100 cation-exchange resin as binding layer, in Chapter 4. The major species was $UO_2(CO_3)_2^{2-}$ (72.88%) and $UO_2(CO_3)_3^{4-}$ (26.70%) in their calculated uranium speciation distribution at pH 8.2. Those results indicated that the apparent lability factor φ_{U_i} and lability factor α_{U_i} of uranium species for DE81 is higher than that for Chelex-100. Since α_{U_i} reflects the

binding ability of uranium on the binding layer, the DE81 anion-exchange filter is more efficient than Chelex-100 for uranium speciation in alkaline waters.

Figure 5.6 Percentage distributions of $\text{UO}_2(\text{CO}_3)_2^{2-}$ (%) as a function of concentration of NaHCO_3 , in uranium-HA model solutions. Uranium concentration $100 \mu\text{g L}^{-1}$, HA concentration 2 mg L^{-1} , NaNO_3 0.01 mol L^{-1} , concentration of NaHCO_3 0.1, 0.5, 1, 2, 5 and 10 mmol L^{-1} . Calculated using Visual MINTEQ program.

Table 5.3 Percentage distribution of uranium species (%) in uranium-HA model solutions, calculated using Visual MINTEQ program. Uranium concentration was 100 $\mu\text{g L}^{-1}$, HA concentration 2 mg L^{-1} , NaNO_3 0.01 mol L^{-1} , NaHCO_3 0.1, 0.5, 1, 2, 5 and 10 mmol L^{-1} , pH is 8. ϕ represents the apparent lability factor of uranium species in these model solutions.

NaHCO ₃ concentration (mmol L ⁻¹)	Percentage of uranium species (%) [*]		
	U-HA	UO ₂ (CO ₃) ₂ ²⁻	UO ₂ (CO ₃) ₃ ⁴⁻
0.1	93.5	0.3	0.0
0.5	78.5	8.8	4.2
1	54.7	19.6	20.1
2	26.0	21.9	50.2
5	8.8	11.2	79.7
10	4.4	5.1	90.5
ϕ	0.62	3.21	0.19

^{*}These values were theoretically calculated by data fitting and the standard deviation was not calculated.

5.4 Conclusions

The effective uranium concentration C_{Ueff} and the percentage of DGT-labile uranium species % L were used to interpret the results obtained from the DGT uptake experiments in model solutions. Apparent lability factor ϕ_{Ui} and the percentage distribution of uranium species θ_{Ui} were used to evaluate the lability of different uranium species. Strong complexing agent (e.g., strong binding sites of HS) reduced the percentage of DGT-labile uranium species, whereas competition between copper and uranium for binding with HS increased the percentage of DGT-labile uranium species. The percentage of uranium DGT-labile species increased with increasing ionic strength in model solutions, indicating that ionic strength might affect the binding of uranium with humic substances. At higher pH, the percentage of DGT-labile uranium species increased because of the formation of U-OH species. With increasing NaHCO_3 concentration, the percentage distribution of $\text{UO}_2(\text{CO}_3)_2^{2-}$ had the same trend as the percentage of DGT-labile uranium species, indicating it had a higher apparent lability factor value ϕ .

5.5 References

1. Warnken, K.W., Davison, W., Zhang, H., Galceran, J., and Puy, J. (2007). In Situ Measurements of Metal Complex Exchange Kinetics in Freshwater. *Environmental Science & Technology* 41, 3179-3185.
2. Buffle, J., Altmann, R.S., Filella, M., and Tessier, A. (1990). Complexation by natural heterogeneous compounds: Site occupation distribution functions, a normalized description of metal complexation. *Geochimica et Cosmochimica Acta* 54, 1535-1553.
3. Filella, M., and Town, R.M. (2001). Heterogeneity and lability of Pb(II) complexation by humic substances: practical interpretation tools. *Fresenius' Journal of Analytical Chemistry* 370, 413-418.
4. Guthrie, J.W., Mandal, R., Salam, M.S.A., Hassan, N.M., Murimboh, J., Chakrabarti, C.L., Back, M.H., and Gregoire, D.C. (2003). Kinetic studies of nickel speciation in model solutions of a well-characterized humic acid using the competing ligand exchange method. *Analytica Chimica Acta* 480, 157-169.
5. Zhang, H., and Davison, W. (1995). Performance Characteristics of Diffusion Gradients in Thin Films for the in Situ Measurement of Trace Metals in Aqueous Solution. *Analytical Chemistry* 67, 3391-3400.
6. Zhang, H., and Davison, W. (1999). Diffusional characteristics of hydrogels used in DGT and DET techniques. *Analytica Chimica Acta* 398, 329-340.
7. Li, W., Zhao, J., Li, C., Kiser, S., and Cornett, R.J. (2006). Speciation measurements of uranium in alkaline waters using diffusive gradients in thin films technique. *Analytica Chimica Acta* 575, 274-280.
8. Morel, F. (1983). Principles of aquatic chemistry. In *Principles of aquatic chemistry*. (New York: J. Wiley), pp. 266-267.
9. Morel, F., and Hering, J.G. (1993). Principles and applications of aquatic chemistry (New York: Wiley).
10. Li, W., Zhao, H., Teasdale, P.R., and Wang, F. (2005). Trace metal speciation measurements in waters by the liquid binding phase DGT device. *Talanta* 67, 571-578.
11. Bolton, K.A., Sjoeborg, S., and Evans, L.J. (1996). Proton binding and cadmium complexation constants for a soil humic acid using a quasi-particle model. *Soil Science Society of America Journal* 60, 1064-1072.
12. Sekaly, A.L.R., Back, M.H., Chakrabarti, C.L., Gregoire, D.C., Lu, J.Y., and Schroeder, W.H. (1998). Measurements and analysis of dissociation rate constants of metal-fulvic acid complexes in aqueous solutions, part II: measurement of decay rates by inductively-coupled plasma mass spectrometry and determination of rate constants for dissociation. *Spectrochimica Acta, Part B: Atomic Spectroscopy* 53B, 847-858.
13. Sekaly, A.L.R., Back, M.H., Chakrabarti, C.L., Gregoire, D.C., Lu, J.Y., and Schroeder, W.H. (1998). Measurements and analysis of dissociation rate constants of metal-fulvic acid complexes in aqueous solutions, part I: simulation of decay curves obtained by inductively coupled plasma-mass spectrometry to evaluate a method to measure the distribution of first-order rate constants. *Spectrochimica Acta, Part B: Atomic Spectroscopy* 53B, 837-846.

14. Pinheiro, J.P., Domingos, R., Lopez, R., Brayner, R., Fievet, F., and Wilkinson, K. (2007). Determination of diffusion coefficients of nanoparticles and humic substances using scanning stripping chronopotentiometry (SSCP). *Colloids and Surfaces, A: Physicochemical and Engineering Aspects* 295, 200-208.
15. Lead, J.R., Wilkinson, K.J., Starchev, K., Canonica, S., and Buffle, J. (2000). Determination of Diffusion Coefficients of Humic Substances by Fluorescence Correlation Spectroscopy: Role of Solution Conditions. *Environmental Science and Technology* 34, 1365-1369.
16. Lenhart, J.J., Cabaniss, S.E., MacCarthy, P., and Honeyman, B.D. (2000). Uranium(VI) complexation with citric, humic and fulvic acids. *Radiochimica Acta* 88, 345-353.
17. Tipping, E. (2002). Cation binding by humic substances. In *Cation binding by humic substances*. (Cambridge, U.K. ; New York: Cambridge University Press), pp. 309-311.
18. Takahashi, Y., Minai, Y., Meguro, Y., Toyoda, S., and Tominaga, T. (1994). Ionic strength and pH dependence of binding constants of Am(III)- and Eu(III)-humates. *Journal of Radioanalytical and Nuclear Chemistry* 186, 129-141.
19. Scally, S., Davison, W., and Zhang, H. (2006). Diffusion coefficients of metals and metal complexes in hydrogels used in diffusive gradients in thin films. *Anal. Chim. Acta* 558, 222-229.
20. Pai, S.C., Whung, P.Y., and Lai, R.L. (1988). Preconcentration efficiency of Chelex-100 resin for heavy metals in seawater. Part 1. Effects of pH and salts on the distribution ratios of heavy metals. *Analytica Chimica Acta* 211, 257-270.

Chapter 6

**Kinetic studies of uranium speciation—
the lability factor α**

6.1 Introduction

The lability factor, α_i , which reflects the affinity of metal species to the DGT binding layers, is the key parameter for evaluating the lability of the DGT-labile species. As defined by Eq. 5.4, the lability factor, α_i , is:

$$\alpha_i = \frac{c_{M_i} - c'_{M_i}}{c_{M_i}}$$

where c_{M_i} is the concentration of metal species in bulk solution, c'_{M_i} is the concentration of metal species on the surface of binding layers. In Chapter 3, the total uranium concentration on the surface of the binding layer has been calculated using linear extrapolation, which may provide valuable information of α .

In this chapter, we try to use competitive ligand exchange method to obtain the lability factor, α , in U-HA systems. Since humic acid (HA) is a heterogeneous system, α presents the percentage of U-HA species that can react with Chelex-100 binding layer during the experimental time.

6.1.1 Competitive Ligand Exchange Method

The kinetic model proposed by Olson and Shuman[1] was adapted to the study of speciation of uranium(VI) complexes as described below. Assuming that a metal complex, ML_i , undergoes a first-order or pseudo-first-order dissociation, as follows:

where M is a metal ion and L_i is a complexant such as CO_3^{2-} or humic acid, $k_{d,i}$ and $k_{f,i}$ are the rate coefficients of dissociation and formation of ML_i , respectively. The charges have been omitted for simplicity.

Assuming also that the metal reacts with a large excess of a competing ligand, e.g., Chelex-100 chelating resin, resulting in the formation of a strong M-Chelex complex:

where $k_{f,\text{M-Chelex}}$ and $k_{d,\text{M-Chelex}}$ are the rate coefficients of formation and dissociation of M-Chelex, respectively. Since the competing ligand has been added in large excess, the net reaction, Eq. 6.3, lies far to the right, and is considered as pseudo-first-order and irreversible

The concentration of ML_i can be described by pseudo-first-order rate law.

$$-\frac{dc_{\text{ML}_i}}{dt} = k_{d,i} c_{\text{ML}_i} \quad (6.4)$$

Integrating Eq. 6.4 and gets Eq. 6.5:

$$c_{\text{ML}_i}(t) = c_{\text{ML}_i}^0 \cdot \exp(-k_{d,i} \cdot t) \quad (6.5)$$

where $c_{\text{ML}_i}^0$ is the initial concentration of the ML_i complex and $c_{\text{ML}_i}(t)$ is the concentration of the ML_i complex at any time, t , and $k_{d,i}$ is dissociation rate coefficient of ML_i .

Since it has been assumed that the ML_i complexes dissociate simultaneously and independently, the total concentration of metal c_M remaining in the solution, at any time, t , is shown by Eq. 6.6

$$c_M(t) = \sum_{i=1}^n c_{ML_i}^0 \cdot \exp(-k_{d,i} \cdot t) \quad (6.6)$$

Considering a M-HA system, Eq. 6.6 can be simplified as consisting of two components: fast (labile) and slow (non-labile) component, and re-written as Eq. 6.7

$$c_M(t) = c_1 \exp(-k_{d1} \cdot t) + c_2 \exp(-k_{d2} \cdot t) \quad (6.7)$$

where c_1 and c_2 are the initial concentrations of the fast and the slow component and k_{d1} and k_{d2} are the dissociation rate coefficients of these components, respectively. The percentage of the total metal remaining in the solution, $C_M(t) = c_M(t)/c_M(0) \times 100\%$, at any time t , was used in this work to avoid the bias error. Eq. 6.7 can be re-written as:

$$C_M(t) = C_1 \exp(-k_{d1} \cdot t) + C_2 \exp(-k_{d2} \cdot t) \quad (6.8)$$

where C_1 and C_2 are the percentage of the fast (labile) and the slow (non-labile) component, respectively, in the initial solution; $C_1 = c_1/c_M(0) \times 100\%$ and $C_2 = c_2/c_M(0) \times 100\%$.

The reaction in the DGT binding experiment is competitive ligand exchange reaction. If we assume all the metal binds with HA and the reaction time is equal to the diffusion time, Δt , which is $\frac{\Delta g^2}{2D}$, according to Eq. 3.18, the percentage of the metal reacts with DGT binding layers is $1 - C_M(\Delta t)$, according to Eq. 6.8. Hence, only the M-HA species that dissociate during the diffusion can react with DGT binding layers and the metal

accumulated on the DGT binding layers during the deployment time, t , can be expressed as:

$$M_{DGT} = \frac{tA}{\Delta g} D_M [1 - C_M(\Delta t)] c_M \quad (6.9)$$

Comparing to Eq. 5.7, the lability factor α is:

$$\alpha = 1 - C_M(\Delta t) = 1 - C_1 \exp(-k_{d1} \cdot \Delta t) - C_2 \exp(-k_{d2} \cdot \Delta t) \quad (6.10)$$

If $-k_{d1} \cdot \Delta t < -k_{d2} \cdot \Delta t \approx 0$, $\alpha = 1 - C_2 = C_1$, the metal species is partial labile; If $-k_{d1} \cdot \Delta t \approx -k_{d2} \cdot \Delta t \approx 0$, $\alpha = 1 - C_1 - C_2 \approx 0$, the species is inert; If $-k_{d1} \cdot \Delta t < -k_{d2} \cdot \Delta t \ll 0$, $\alpha \approx 1$, the species is fully labile. The objective of this Chapter is to obtain C_1 , C_2 , k_{d1} and k_{d2} in different model solutions.

6.2 Experimental

6.2.1 Reagents

Chelex-100 chelating resin (Bio-Rad 100-200 mesh) was conditioned for this work by soaking Chelex-100 resin sequentially in methanol, 1 mol L⁻¹ HCl, 3 mol L⁻¹ NH₄OH and 0.1 mol L⁻¹ HCl[2]. The ICP-MS/AES uranium standard solution (SCP SCIENCE, 1000 mg L⁻¹) was used to prepare uranium model solutions. All sample solutions were prepared with deionized water of resistivity of 18.2 MΩ-cm, obtained direct from a NANOpure Diamond Ultrapure Water System (Barnstead, USA). Nitric acid (Optima, Fisher Scientific) and sodium hydroxide (Caledon Laboratories LTD) were used to adjust

the pH. Ammonium acetate (BDH Inc.) was used to prepare 0.01 mol L^{-1} ammonium acetate solutions.

Humic acid was supplied by Dr. Les Evans (University of Guelph, Guelph, Ontario), who characterized and purified the HA according to the procedure recommended by the International Humic Substances Society. The bidentate complexing capacity of HA was calculated to be 4.88 mmol/g [3]. A stock solution of 1.0 g L^{-1} HA was prepared by dissolving approximately 1.0 g HA in sodium hydroxide, and the solution was made up to 1 L with ultrapure water. The solution was stored in the dark at 4°C .

6.2.2 Model solutions and synthetic fresh water samples

A series of model solutions were prepared by spiking known amounts of uranium standard solution into the HA solutions to make the concentration ratio of $\text{U(VI)}/\text{HA}$ 0.1 , 0.01 and 0.001 . The total uranium concentration in these solutions was fixed at $20 \mu\text{g L}^{-1}$ ($8.4 \times 10^{-8} \text{ mol L}^{-1}$), whereas the HA concentration was varied: 0.2 , 2.0 and 20 mg L^{-1} . The above concentration range corresponded to the range found in natural waters. Ammonium acetate was added to those model solutions as pH buffer (final concentration 0.01 mol L^{-1}). The mole/mass ratio of $\text{U(VI)}/\text{HA}$ in the above three model solutions was 0.42 , 0.042 and 0.0042 mmol/g . The pH of these model solutions was adjusted to 6.0 , 7.0 or 8.0 , using aqueous solutions of NaOH and HNO_3 . The model solutions were then equilibrated for 48 hours in the dark at room temperature.

The synthetic fresh water sample simulating the natural lake water was prepared in our laboratory by adding inorganic chemicals and humic acid to ultrapure water of resistivity $18 \text{ M}\Omega\text{-cm}$.

6.2.3 Natural water samples

Samples of natural waters (surface waters) were collected from St. Lawrence River at Morrisburg (Ontario, Canada), using 2.2 L Teflon bottles. Major cations and anions were quantitatively determined by using Atomic Emission Spectrometry (AES) and Ion-Exchange Chromatography (IEC), respectively. Total dissolved organic carbon and inorganic carbon were determined using TOC Analyzer (Shimadzu TOV-V_{CPH}).

6.2.4 Ligand exchange experiment

300 mL of the test sample of above solutions was stirred with a Teflon-coated magnetic stirring bar in a Teflon reactor. About 3 gram Chelex 100 resin (1g/100mL), which had been soaked in 0.01 mol L⁻¹ ammonium acetate buffer at the same pH as that of the test sample solution, was added to the test sample. The test sample was filtered with a 8µm polycarbonate membrane filter (Whatman), which was placed at the end of the reactor tube to filter out the Chelex 100 resin before introducing the filtrate into Elan 6100 DRC ICP-MS(PerkinElmer SCIEX), as shown in Figure 6.1. The total experimental time was 1 to 2 hours.

Figure 6.1 Diagram of CLEM experiment.

6.3 Results and discussion

The U(VI)-HA systems were very complex, even in a simple model solution. The complexation kinetics of U(VI)-HA could be influenced by many factors, such as the deprotonation of HA at different pH, the hydrolysis of uranyl ion and the formation of uranyl complexes. The experimental data were analyzed using Marquardt-Levenberg algorithm, an advanced Non-Linear Regression algorithm. All the data were fitted using one, two or three distinct components to find the best-fitting curve, using SigmaPlot 10 computer program (Systat Software Inc.).

The kinetic curves and kinetically distinguishable components are presented in Figures 6.2-6.4 and Tables 6.1-6.3. The error bars in the figures represent the standard deviation of the average of three measurements. In the kinetic curves, the initial steep part represents the fast component, which is the labile fraction (C_1), whereas the plateau part is the slow component or non-labile fraction (C_2). As reported by Sekaly et al.[4, 5], the binding sites of humic substances can be differentiated into recognizable groups, approximated by a small collection of rate coefficients. The binding sites of heterogeneous, natural organic complexants, such as humic substances, have continuous distributions and it is therefore impossible to define the individual binding sites. Two kinetically distinguishable components (fast and slow) were found to be the best fitting for the data.

6.3.1 Effect of the U(VI)/HA ratio on kinetic parameters

Figure 6.2 presents the ligand exchange kinetics for the three U(VI)/HA ratios in model solutions at pH 6.0. The data for the other pH values are not shown. Table 6.1 presents the kinetically distinguishable components obtained by fitting the data for all the pH values to the Kinetic Model. The concentration of uranium bound to strong binding sites of humic acid (slow or non-labile component) increased with decreasing U(VI)/HA ratio at all pH values, whereas the concentration of uranium bound to weak binding sites (fast or labile component) decreased. The dissociation rate coefficients of U(VI) bound to humic acids decreased with decreasing U(VI)/HA ratios, probably because uranium was bound to stronger binding sites at lower U(VI)/HA ratios. Saito et al. [6] reported two apparent complex formation constants for uranium-humic acid complexes, indicating two

different types of binding sites for uranium in humic acid. However, the rate coefficients (k_{d1} and k_{d2}) do not correspond to two precisely defined binding sites or complexes because there is a large number of binding sites in humic acid and the physical and chemical nature of the sites vary widely. Hence, the rate coefficients probably represent the average dissociation coefficient of similar binding sites. When the HA concentration is 0.2 mg L^{-1} , in the presence of atmospheric CO_2 , the major uranium species are U-HA, U-carbonate, U-OH and U-acetate species. The labile fractions (fast) are probably the inorganic uranium species and the uranium binding with weak HA binding sites.

The first-order dissociation rate coefficient of the fast kinetically distinguishable component (k_{d1}) is around 10^{-3} s^{-1} , whereas that of the slow component (k_{d2}) is about 10^{-5} s^{-1} . Compared to the previous studies on nickel-HA model solutions[7], the first-order dissociation rate coefficients of uranium are higher than that of nickel, which are about 10^{-4} s^{-1} (fast), and 10^{-6} s^{-1} (slow), suggesting that the UO_2^{2+} binds less strongly than Ni^{2+} to humic acid.

Figure 6.2 Ligand exchange kinetics for three U(VI)/HA ratios in model solutions at pH 6.0. Uranium concentration was $20 \mu\text{g L}^{-1}$ ($8.4 \times 10^{-8} \text{ mol L}^{-1}$) and ammonium acetate concentration was 0.01 mol L^{-1} , whereas humic acid concentration was varied.

◆: U/HA ratio 0.1, HA 0.2 mg L^{-1}

▲: U/HA ratio 0.01, HA 2.0 mg L^{-1}

■: U/HA ratio 0.001, HA 20.0 mg L^{-1} .

Table 6.1 Kinetically distinguishable components in U(VI)-HA model solutions, ammonium acetate concentration 0.01 mol L^{-1} , uranium concentration $20 \text{ } \mu\text{g L}^{-1}$

U/HA ratio	pH	$C_1 (\%)$	$k_{d1} (10^{-3} \text{ s}^{-1})$	$C_2 (\%)$	$k_{d2} (10^{-5} \text{ s}^{-1})$
0.1	6	50.2 ± 5.6	2.0 ± 0.1	44.6 ± 2.7	15.3 ± 0.5
	7	58.1 ± 5.4	2.3 ± 1.0	34.6 ± 12.4	12.7 ± 11.5
	8	78.5 ± 6.7	2.5 ± 0.4	20.9 ± 0.9	7.4 ± 1.4
0.01	6	31.2 ± 1.6	0.6 ± 0.04	62.6 ± 0.7	9.4 ± 0.6
	7	24.0 ± 2.7	0.6 ± 0.1	66.7 ± 3.0	9.9 ± 0.5
	8	26.2 ± 4.7	0.4 ± 0.1	71.6 ± 5.7	6.6 ± 1.0
0.001	6			94.0 ± 3.4	4.3 ± 0.8
	7			82.3 ± 3.1	3.3 ± 0.5
	8			83.1 ± 5.1	2.8 ± 0.5

The ionic strength in the above model solutions was about 0.01 mol L^{-1} . When the U/HA ratio is 0.01, at pH 7, C_1 is 24% (Table 6.1). This result is now compared to the DGT results in Chapter 5, Figure 5.3, where the ionic strength and pH were the same values as this study. In Chapter 5, Figure 5.3, when the HA concentration was 10 mg L^{-1} and uranium concentration was $100 \text{ } \mu\text{g L}^{-1}$ (U/HA ratio 0.01), the percentage DGT-labile fraction, %L, was about 9%. The diffusion coefficients of $D_{\text{U-HA}}$ obtained in Chapter 3 is $4.9 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$ and the thickness of the diffusive layer, Δg , is 0.04 cm. The diffusion time Δt is about 1,600s, according to Eq. 3.18. Since $-k_{d1} \cdot \Delta t < -k_{d2} \cdot \Delta t \approx 0$, the lability factor $\alpha_{\text{U-HA}}$ should be equal to C_1 , according to Eq. 6.10.

If we simply assume there is only one U-HA species in the model solutions, the percentage distribution of uranium species, θ_{U-HA} is 100%. Therefore the percentage of DGT-labile uranium species, %L, is equal to the apparent labailty factor, ϕ_{U-HA} . According Eq. 5.11, $\%L = \phi_{U-HA} = \frac{D_{U-HA}\alpha_{U-HA}}{D_U\alpha_U}$, and the lability factor, $\alpha_{U-HA} = \frac{\%L \times D_U \times \alpha_U}{D_{U-HA}}$, as we discussed in Chapter 5. The overall diffusion coefficient of uranium, D_U , is $1.5 \times 10^{-5} \text{ cm}^2\text{s}^{-1}$ and the diffusion coefficient of U-HA, D_{U-HA} is $4.9 \times 10^{-7} \text{ cm}^2\text{s}^{-1}$. If α_U is considered as 1, the lability factor of U-HA is 27%. The lability factor of U-HA, α_{U-HA} , calculated using DGT data, is close to C_1 (24%), indicating that the percentage of kinetic labile fraction, C_1 , can be used as labile factor α_{U-HA} , when the U/HA ratio is 0.01, and the U-HA species is partial labile.

To study the effect of pH buffer on the kinetics parameters of U-HA complexes, U(VI) model solutions with the ammonium acetate buffer and without the buffer were investigated using CLEM. Table 6.2 presents the kinetic parameters for uranium in 0.01 mol L⁻¹ ammonium acetate buffer and U(VI)-HA model solution without pH buffer, at pH 7.0. The ‘labile’ and the ‘non-labile’ fraction can be obtained from the data fitting, which may, however, interfere with the determination of speciation parameters of U-HA. The “labile fraction” of uranium in the ammonium acetate buffer is much greater than that in the U(VI)-HA model solution without the buffer. The rate coefficients for both fast and slow components in the ammonium acetate buffer are about 10 times higher than those in the U(VI)-HA model solution without the buffer, which indicates that the uranium species in ammonium acetate buffer is more labile than that in U-HA model solution. The ammonium acetate buffer can affect the results of the uranium kinetic

speciation. Compared with the data of U(VI)-HA model solution with the buffer at pH 7.0 in Table 6.1, the labile component in the U(VI)-HA model solution with the buffer is greater than that without the buffer, probably because of the formation of uranium-acetate complex in the U(VI)-HA model solution with the buffer. The uranium bound to weak binding sites of humic acid and uranium-acetate complex are not distinguishable in CLEM, probably because the dissociation rate coefficients of the two uranium complex are close. Table 6.2 also shows the kinetic parameters for uranium in 0.004 mol L⁻¹ sodium bicarbonate. Uranium-carbonate species predominate in the presence of bicarbonate and carbonate, and in CLEM experiment these species are identified as labile species.

Table 6.2 Kinetically distinguishable components in U(VI)-HA model solutions without the ammonium acetate buffer, pH 7.0; uranium in 0.01 mol L⁻¹ ammonium acetate buffer, pH 7.0; and uranium in 0.004 mol L⁻¹ sodium bicarbonate, pH 10. Uranium concentration 20 µg L⁻¹

U/HA ratio	C ₁ (%)	k _{d1} (10 ⁻³ s ⁻¹)	C ₂ (%)	k _{d2} (10 ⁻⁵ s ⁻¹)
0.1	46.3±3.1	1.1±0.2	51.3±1.6	11.9±1.9
0.01	16.6±2.3	2.4±2.2	77.1±6.3	10.3±2.6
0.001	3.2±1.3	1.8±0.8	95.4±2.1	4.9±0.5
U, buffer only	73.1±10.6	10.5±3.7	25.3±10.8	46.3±3.5
U, NaHCO ₃	90.8±10.5	19.9±4.7	20.4±4.9	20.6±6.5

6.3.2 Effect of pH on kinetic parameters

There is no significant pH effect on the kinetic parameters in the model solutions containing the U (VI)/HA ratio 0.01 and 0.001. However, at the U (VI)/HA ratio 0.1, as pH values increases from 6.0 to 8.0, the labile component increases with a corresponding decrease in the non-labile component. Guthrie et al.[7] reported an opposite trend in their kinetic studies of Ni(II)/HA: the labile component of Ni(II)-HA decreased with the increasing of pH probably because of the deprotonation of binding sites in humic acid at higher pH. Figure 6.3 presents the ligand exchange kinetics for U(VI)/HA in model solutions containing the U(VI)/HA ratio 0.1 at different pH values. In freshwater systems, free uranyl ion (UO_2^{2+}) is the predominant species only at low pH. With increasing pH, the proportions of hydrolysis products of U(VI) and U-carbonate species increase. In the kinetic study, formation of uranium-hydroxide decreases the percentage of non-labile component and increases the percentage of labile component. At the U(VI)/HA ratio 0.1, this effect could be more significant than at lower U(VI)/HA ratios because an increase in the HA concentration suppresses the hydrolysis of U(VI) and promotes the formation of U(VI)-HA complex[8]. Furthermore, at the lower U(VI)/HA ratios, a greater proportion of uranium binds to the strong binding sites, resulting in an increase in the non-labile fraction.

6.3.3 Kinetic Parameters in the Natural Waters and the Synthetic fresh Water Sample

The total uranium concentration in the St. Lawrence River water (Ontario, Canada) sample was $0.35 \pm 0.01 \mu\text{g L}^{-1}$ (determined by ICP-MS), which was too low to give a signal strong enough to do the computer program fitting. Therefore, the natural water sample and synthetic fresh water sample were spiked with uranium standard solution so as to produce the final concentration of $10 \mu\text{g L}^{-1}$ of uranium. The pH value of St. Lawrence River water sample was 8.3, whereas that of synthetic fresh water sample was 7.8. Figure 6.4 presents ligand exchange kinetics of uranium species in the uranium-spiked samples of St. Lawrence River water and the synthetic fresh water. In the kinetic runs, the percentage of uranium remaining in both the St. Lawrence River water sample and the synthetic fresh water sample decreased very quickly to about 5% and 20%, respectively, in the first 2000s of the experiment. At the end of experiment, the uranium remaining in the St. Lawrence River water sample was almost 1%, whereas the uranium remaining in synthetic fresh water sample was about 5%.

The major inorganic cations and anions of these two samples are presented in Table 6.3 as well as total organic carbon (TOC) and total inorganic carbon (TIC). The kinetically distinguishable components of uranium species in the two samples are presented in Table 6.4. The labile components in the two samples were greater than 90% of all uranium species, and only the tightly bound uranium remained after 4000s, indicating that the dissociation rate coefficients of slow components were very small (less than 10^{-6}s^{-1}); these components were considered as inert. There are many factors, such as the number

and type of ligands, the position of the binding sites in the structure of the complexants, the metal-to-binding site ratio, and the pH[9], can affect the binding capacity and affinity of the heterogeneous complexants such as HA and FA for metal binding. In pH range of 6 to 8, $\text{UO}_2(\text{OH})\text{-HA(I)}$ complex is dominant in the absence of CO_2 , as reported by Sachs using laser-induced fluorescence spectroscopy, where HA(I) means that one proton exchanging functional groups of HA takes part in the reaction[8]. However, under usual environmental conditions, at high pH, hardness and alkalinity, the uranium-carbonate and uranium-hydroxide-carbonate become the dominant species[10].

Figure 6.5 presents the predicted distribution of uranium species as a function of pH (2 to 12) in synthetic fresh water sample, calculated using Visual MINTEQ program. At pH 7.8, about 92% uranium species is $\text{Ca}_2\text{UO}_2(\text{CO}_3)_3(\text{aq.})$, whereas U-HA species is about 3%. Therefore, the U/HA ratio of U-HA species in the synthetic fresh sample is about 0.0003. The non-labile uranium species is probably the uranium bound to the strong binding sites of humic acid. For the St. Lawrence River water sample, the pH and the concentration of CO_3^{2-} are higher than that of the synthetic fresh water sample, and about 97% of total uranium is U-carbonate species in spite of the fact that it has a higher DOC concentration (2.8 mg L^{-1}).

Figure 6.3 Ligand exchange kinetics for U(VI)/HA in model solutions with U(VI)/HA ratio 0.1 at different pH values. Uranium concentration was $20 \mu\text{g L}^{-1}$ ($8.4 \times 10^{-8} \text{ mol L}^{-1}$), HA concentration is 0.2 mg L^{-1} , ammonium acetate 0.01 mol L^{-1} .

■: pH 6.0, ▲: pH 7.0, ◆: pH 8.0.

Figure 6.4 Ligand exchange kinetics of uranium species in St. Laurence River and synthetic fresh water samples. Uranium concentration was $10 \mu\text{g L}^{-1}$.

■: synthetic fresh water;

◆: St. Laurence River water samples.

Table 6.3 Major inorganic ions, total organic and inorganic carbon in St. Lawrence River and in synthetic fresh water samples

	St. Lawrence River sample (mg L ⁻¹)	Synthetic fresh water sample (mg L ⁻¹)
Ca ²⁺	41.9±0.3	35.2*
Mg ²⁺	8.8±0.8	8.9
Na ⁺	20.2±0.3	19
K ⁺	2.5±0.2	1.7
SO ₄ ²⁻	26.6±0.2	35.5
NO ₃ ⁻	0.55±0.03	2.8
Cl ⁻	33.7±0.4	62
TOC	2.8±0.5	N/A
TIC	19.9±0.4	N/A
HCO ₃ ⁻	N/A	50
Humic acid	N/A	1

*The synthetic fresh water sample was prepared from reagent grade chemicals and the standard deviation was not measured.

Table 6.4 Kinetically distinguishable components of uranium species in St. Lawrence River water and in synthetic fresh water samples. The uranium concentration was $10 \mu\text{g L}^{-1}$

	C_1 (%)	k_{d1} (10^{-3}s^{-1})	C_2 (%)	k_{d2} (10^{-5}s^{-1})
St. Lawrence River	94.3 ± 1.8	2.7 ± 2.8	5.1 ± 3.0	$< 10^{-6}$ (Inert)
Synthetic fresh water	91.0 ± 12.8	0.6 ± 0.1	11.8 ± 9.8	$< 10^{-6}$ (Inert)

Li et al. [11] studied the uranium speciation in St. Lawrence River using Diffusive Gradients in Thin Films (DGT) technique and reported that the DGT labile fraction was about 73% for the DE81 anion-exchange filter and 60% for the Chelex DGT cation-exchange resin. In their study, the major uranium species was $\text{UO}_2(\text{CO}_3)_2^{2-}$ (72.88%) and $\text{UO}_2(\text{CO}_3)_3^{4-}$ (26.70%) in the calculated uranium speciation distribution at pH 8.2; therefore, the DGT labile species for DE 81 was most likely $\text{UO}_2(\text{CO}_3)_2^{2-}$. The labile component in our study was most probably uranium-carbonate species, whereas the non-labile component was the uranium bound to the strong binding sites of DOC.

Figure 6.5 Predicted uranium speciation (% total uranium) in synthetic fresh water as function of pH (2 to 12) calculated using Visual MINTEQ ver 2.51. Total uranium concentration $10 \mu\text{g L}^{-1}$, major cation and anion concentrations are shown in Table 6.3.

□: UO_2^{2+} ; ◇: HA-UO_2^+ ; △: HA-UO_2 ; ×: $\text{UO}_2\text{CO}_3(\text{aq.})$;
 ◆: $\text{Ca}_2\text{UO}_2(\text{CO}_3)_3(\text{aq.})$; ■: $\text{UO}_2(\text{OH})_3^-$; ▲: $\text{UO}_2(\text{OH})_4^{2-}$

6.3.4 Adjunctive and Disjunctive Pathways

If the metal species is inert, such as uranium bound with the strong binding sites of HA, which cannot dissociate during the diffusion time, Δt , it can react with DGT binding layer directly. In CLEM, two reaction pathways for the overall ligand-exchange reactions may be considered:

- i) Slow dissociation of ML to give M and L, followed by a fast reaction with the competitive ligand, Chelex 100, which is known as the Disjunctive Pathway, shown in Eq. 6.1 and Eq. 6.2
- ii) Direct attack by the competitive ligand followed by loss of the original ligand, L, which is called the Adjunctive Pathway, shown in Eq. 6.11 and Eq. 6.12.

Both the Disjunctive and the Adjunctive Pathway may contribute to the observed overall rate coefficient.

The metal binding to Chelex-100 resin is a surface reaction. If the reaction is simplified as unimolecular adsorption reaction, it can be treated in terms of the Langmuir Isotherm as follows[12].

$$K = k_a / k_{-a} \quad (6.14)$$

$$\theta = \frac{K[M]}{1 + K[M]} \quad (6.15)$$

$$v = k\theta = \frac{kK[M]}{1 + K[M]} \quad (6.16)$$

where M is metal ions, S is the binding sites, k_a is the rate coefficient for the forward reaction, k_a is rate coefficient for the reverse reaction, and K is equilibrium constant for the adsorption process. The rate v is proportional to θ , which is the fraction of the surface that is covered. If the concentration of M is high, the surface is well covered, $\theta \approx 1$, $v = k$, and the kinetics is zeroth order. If the concentration of M is low, $K[M] \approx 0$, the surface is sparsely covered, $v = k\theta = kK[M]$ and the kinetics is first-order.

The pore size of Chelex-100 resin, which is about 1.5nm[13], is smaller than the size of humic acid, whose hydrodynamic radii range from 2-7 nm [14]. In CLEM experiments, free metal ions can bind with both the internal binding sites and surface binding sites of Chelex-100 resin, whereas the larger metal-humic acid complexes can only react with the surface binding sites of the Chelex-100 resin. The binding of free metal ions on surface binding sites of Chelex-100 can be ignored because the surface binding sites contribute little to the total adsorptive capacity of the resin [15]. Since the internal binding sites in Chelex-100 resin are in excess of the free metal ions, the binding of free metal ions follows the first-order kinetics. However, the surface binding sites of Chelex-100 resin are limited to metal humic substances complexes, so the reaction of U-HA complex with Chelex-100, which can only occur on the surface, follows zeroth order kinetics.

To validate the above hypothesis, different concentrations of Chelex-100 resin (1g/100mL, 2g/100mL and 3g/100mL) were tested in model solutions having U(VI)/HA ratio 0.001. As shown in Figure 6.6, as more Chelex-100 was added to the model solution, the reaction rate coefficient increased, indicating that the rate coefficient was dependent on the concentration of Chelex-100. Therefore, as the U/HA ratio is very small, the Adjunctive Pathway is predominant. Since the surface of Chelex-100 resin is limited and is fully covered by U-HA complexes, the kinetics is zeroth order.

The rate coefficient of zeroth order kinetics (Adjunctive Pathway), is represented by Eq. 6.17 and Eq. 6.18

$$-\frac{dC_{ML}}{dt} = k \quad (6.17)$$

$$C_{ML}(t) = C_{ML}^0 - k \cdot t = 1 - k \cdot t \quad (6.18)$$

where $C_{ML}(t)$ is the percentage of uranium remaining in the sample solution, at any time t , C_{ML}^0 is the initial C_{ML} at time 0, which is expected to be 100%, and k is the rate coefficient. In DGT experiment, if the metal species is inert and the average reaction time on the DGT binding layers, t , is considered as the diffusion time, Δt , the lability factor $\alpha = 1 - C_{ML}(\Delta t) = 1 - (1 - k \cdot \Delta t) = k \cdot \Delta t$, according to Eq. 6.10 and 6.18.

The data of ligand exchange kinetics for U-HA in model solutions having the U(VI)/HA ratio 0.001 at three pH values are fitted to Eq. 6.18. The rate coefficients for pH 6, 7 and 8 are $4.1 \times 10^{-3} \% s^{-1}$, $3.5 \times 10^{-3} \% s^{-1}$ and $3.3 \times 10^{-3} \% s^{-1}$, whereas the initial percentage of

U-HA complexes for the three pHs are 94.8%, 90.7% and 92.6%, respectively, indicating there was probably only one component (non-labile) in U-HA complexes at the U/HA ratio 0.001. In the case of zeroth order kinetics, the CLEM with Chelex-100 as the competitive ligand is not able to determine the dissociation rate coefficient of complexes of metal-humic substance.

Figure 6.6 Ligand exchange kinetics for U(VI)/HA in model solutions when U(VI)/HA ratio is 0.001. Uranium concentration was $20 \mu\text{g L}^{-1}$ ($8.4 \times 10^{-8} \text{ mol L}^{-1}$), HA concentration is 20 mg L^{-1} , ammonium acetate 0.01 mol L^{-1} .
 ◆: Chelex-100 1g/100mL;
 ■: Chelex-100 2g/100mL;
 ▲: Chelex-100 3g/100mL

6.4 Conclusions

The uranium speciation of every sample was characterized either as a “labile” or a “non-labile” uranium complex depending on the dissociation rate coefficients of the complexes. The results showed that as the U(VI)/HA ratio was decreased, the dissociation rate coefficients decreased and the labile fraction decreased as well. When the U(VI)/HA ratio was 0.1, the labile fraction of the U(VI)-HA increased with increasing pH; however, there was no pH effect on the dissociation of U(VI)-HA complexes at lower U(VI)/HA ratios. Chelex-100 had some limitations in its use for the study of dissociation of U-HA complex at very low U(VI)/HA ratios because CLEM is not able to provide us the dissociation coefficient in the case of adjunctive pathway at very low U(VI)/HA ratios. The atmospheric CO₂ may affect the CLEM experiments when HA concentration is 0.2 mg L⁻¹. The U-carbonate species can be considered as labile fraction and cannot be distinguished from other labile species such as U-hydroxide and U binding with the weak binding sites of HA.

6.5 References

1. Olson, D.L., and Shuman, M.S. (1985). Copper dissociation from estuarine humic materials. *Geochimica et Cosmochimica Acta* 49, 1371-1375.
2. Price, N.M., Harrison, G.I., Hering, J.G., Hudson, R.J., Nirel, P.M.V., and Morel, F.M.M. (1989). Preparation and chemistry of the artificial algal culture medium Aquil. *Biological Oceanography* 6, 443-461.
3. Bolton, K.A., Sjoeborg, S., and Evans, L.J. (1996). Proton binding and cadmium complexation constants for a soil humic acid using a quasi-particle model. *Soil Science Society of America Journal* 60, 1064-1072.
4. Sekaly, A.L.R., Back, M.H., Chakrabarti, C.L., Gregoire, D.C., Lu, J.Y., and Schroeder, W.H. (1998). Measurements and analysis of dissociation rate constants of metal-fulvic acid complexes in aqueous solutions, part II: measurement of decay rates by inductively-coupled plasma mass spectrometry and determination of rate constants for dissociation. *Spectrochimica Acta, Part B: Atomic Spectroscopy* 53B, 847-858.
5. Sekaly, A.L.R., Back, M.H., Chakrabarti, C.L., Gregoire, D.C., Lu, J.Y., and Schroeder, W.H. (1998). Measurements and analysis of dissociation rate constants of metal-fulvic acid complexes in aqueous solutions, part I: simulation of decay curves obtained by inductively coupled plasma-mass spectrometry to evaluate a method to measure the distribution of first-order rate constants. *Spectrochimica Acta, Part B: Atomic Spectroscopy* 53B, 837-846.
6. Saito, T., Nagasaki, S., and Tanaka, S. (2002). Evaluation of the complexation behavior between humic acid and UO_2^{2+} with fluorescence spectroscopy and its mixture analysis. *Radiochimica Acta* 90, 27-33.
7. Guthrie, J.W., Mandal, R., Salam, M.S.A., Hassan, N.M., Murimboh, J., Chakrabarti, C.L., Back, M.H., and Gregoire, D.C. (2003). Kinetic studies of nickel speciation in model solutions of a well-characterized humic acid using the competing ligand exchange method. *Analytica Chimica Acta* 480, 157-169.
8. Sachs, S., Brendler, V., and Geipel, G. (2007). Uranium(VI) complexation by humic acid under neutral pH conditions studied by laser-induced fluorescence spectroscopy. *Radiochimica Acta* 95, 103-110.
9. Chakraborty, P., Gopalapillai, Y., Murimboh, J., Fafous, I.I., and Chakrabarti, C.L. (2006). Kinetic speciation of nickel in mining and municipal effluents. *Analytical and Bioanalytical Chemistry* 386, 1803-1813.
10. Markich, S.J. (2002). Uranium speciation and bioavailability in aquatic systems: An overview. *TheScientificWorld* [online computer file] 2, 707-729.
11. Li, W., Zhao, J., Li, C., Kiser, S., and Cornett, R.J. (2006). Speciation measurements of uranium in alkaline waters using diffusive gradients in thin films technique. *Analytica Chimica Acta* 575, 274-280.
12. Laidler, K.J. (1987). Chemical kinetics. In *Chemical kinetics*, 3rd Edition. (New York: Harper & Row), pp. 229-245.
13. Florence, T.M. (1977). Trace metal species in fresh waters. *Water Research* 11, 681-687.

14. Kawahigashi, M., Sumida, H., and Yamamoto, K. (2005). Size and shape of soil humic acids estimated by viscosity and molecular weight. *Journal of Colloid and Interface Science* 284, 463-469.
15. Tessier, A., and Turner, D.R. (1995). Metal speciation and bioavailability in aquatic systems. In *Metal speciation and bioavailability in aquatic systems*. (New York: John Wiley), pp. 262-263.

Chapter 7

**Development of DGT device by
applying electric potential**

7.1 Introduction

7.1.1 Limitations of the current DGT technology

One important application of DGT is *in-situ* preconcentration. However since the concentration of uranium in unpolluted natural waters is extremely low (typically total uranium concentration is less than $1 \mu\text{g L}^{-1}$ [1]), the requirement for setting the time-period for deployment of the DGT becomes excessively long (several days[2, 3]) because of the low diffusion coefficients of uranium species. To overcome these limitations, the development of an improved version of the DGT using an applied electric potential to accelerate mass transport was undertaken.

7.1.2 Theory

DGT simulates a passive transport process in bio-membrane. Two processes are involved in DGT: diffusion through the diffusive gel layer and binding of metals by the binding layer. The driving force of mass flux is the concentration difference between the metal species in natural water systems and that on the surface of binding layer, which is controlled by the binding kinetics of the binding layers, as discussed earlier.

If an electric potential is applied to the DGT, the generated electric field attracts the oppositely charged ions and repels the like charges —the result is accelerated mass-transport, and hence, the metal flux increases. Since energy is involved in the transport process, the new DGT devices might be used to mimic an active transport process.

The flux is defined as a vector and mass flow occurs down a concentration gradient, as expressed by Fick's first law of diffusion:

$$J = -D \frac{dc}{dl} \quad (7.1)$$

where J is flux, D is diffusion coefficient; c is the concentration of metal ions and l is the distance, dc/dl is the concentration gradient.

Under an applied electric field on the DGT device, the flux (J) of metal ions is:

$$J = -D \frac{dc}{dl} - u \frac{d\phi}{dl} c_b \quad (7.2)$$

In the right-hand side of Eq. 7.2, the first term is the same as Fick's first law and the second term is the ion flow moving down an electric field gradient, where u is the mobility of metal ion, c_b is the metal ion concentration in bulk solution, and $d\phi/dl$ is the electric field gradient[4].

The mass flux in the diffusive gel can be described as

$$J = -D \frac{c_b - c_0}{\Delta g} - u \frac{\Delta\phi}{\Delta g} c_b \quad (7.3)$$

If the metal species concentration is assumed as zero, i.e., c_0 is negligible, on the surface of DGT binding layer (ideal DGT binding layer), the flux (J) can be expressed as:

$$J = -\frac{c_b}{\Delta g} (D + u\Delta\phi) \quad (7.4)$$

The metal uptake M by DGT binding layer can be calculated as:

$$M = \frac{c_b}{\Delta g} (D + u\Delta\phi) \times t \times A \quad (7.5)$$

$\Delta\phi$ is directly proportional to the applied voltage, U, as shown:

$$\Delta\phi = \sigma U \quad (7.6)$$

where σ is defined as an electrode parameter, which is dependence of the electric field properties (the shape of the electrodes, the distance between two electrodes, and other factors.) u and σ are constants in a given system. If we define electric field parameter, κ , as $\kappa = u\sigma$, then Eq. 7.5 can be simplified as:

$$M = \frac{c_b}{\Delta g} (D + \kappa U) \times t \times A \quad (7.7)$$

To obtain the parameter, κ , the slope of the linear curve of M versus U can be used. The slope is equal to $\frac{c_b}{\Delta g} t A \kappa$. As we know the electric field parameter, κ , the concentration of bulk solution can be calculated using Eq. 7.8.

$$c_b = \frac{M \Delta g}{(D + \kappa U) \times t \times A} \quad (7.8)$$

In routine application at a given temperature, Δg , A , t and U can be maintained constant and a calibration plot of M versus the bulk concentration, c_b , can be used to calculate the concentration of unknown samples. The attractive feature of the new DGT device is its ability of *in-situ* pre-concentration. The accumulated metal ions (oppositely charged) in the resin layer increases as the applied potential is increased and the pre-concentration factor can be adjusted by the variable applied potential. Another feature of the new DGT device is that it can selectively measure metal species according to its charge and mobility. Since in natural waters, a large portion of uranium species are anionic forms, positive potential has been applied for *in-situ* analysis of uranium using the new DGT device.

7.2 Experimental

7.2.1 Instrument

An electric potential was applied using a computer-controlled Autolab PGSTAT 30 potentiostat/galvanostat (Eco. Chemie BV, The Netherlands) with a Metrohm 663 VA stand (Metrohm, Switzerland). The reference electrode was Ag/AgCl electrode in a glass tube filled with 3 mol L⁻¹ KCl and fitted with a porous Vycor tip (Bioanalytical Systems, Inc., USA). The counter electrode (auxiliary electrode) was made of a platinum rod (Metrohm, Switzerland).

7.2.2 Preparation of polyacrylamide gel and Chelex-100 resin gel

The polyacrylamide gel and Chelex-100 resin gel were prepared following the procedures described earlier in Chapter 2. The thickness the diffusive gel layer was 0.04 cm.

7.2.3 Assembly of the New DGT device

The DGT diffusive gel layer, Chelex-100 resin gel and filter membrane were all cut 11 mm in diameter to fit a cap with a window of 7 mm in diameter. The cellulose filter membrane, diffusive gel, Chelex-100 resin gel, another filter membrane and a sealing ring were placed in the above order in the cap (Figure 7.1). A tube was inserted into the cap and the DGT device was fully sealed with the sealing ring. Then a platinum electrode was placed in the tube.

Figure 7.1 New DGT device Assembly (step 1)

Figure 7.2 New DGT device Assembly (step 2)

Platinum auxiliary electrode, gel electrode and calomel reference electrode were placed into the cap of a VA stand (Figure 7.2). 1 mL NaNO_3 (0.01 mol/L) was added into the gel electrode as gel electrode solution. Then the three electrodes were connected with Autolab potentiostat (Figure 7.3).

Figure 7.3 New DGT device Assembly (step 3)

7.2.4 Experimental procedure

The voltammetric cell was filled with model solutions (75 mL). The platinum auxiliary electrode, the gel electrode and the calomel reference electrode were placed to reach below the surface of the sample solution. The applied potential (deposition potential) was set from -9V to 9V, and the experimental time was 0.5-4 hours. After the end of the

experiment, Chelex-100 binding gel layer was removed from the gel electrode and the uranium was eluted using 20% (v/v) HNO₃. The concentration of uranium in the eluted sample and in gel electrode solution was determined using Elan-6100 ICP-MS.

7.3 Results and discussion

7.3.1 Uranium in gel electrode solution

Since the platinum electrode is placed in gel electrode solution, it is inevitable that the uranium species pass through the binding layers and move into the gel solution under the applied electric field, resulting in the lower uranium uptake by the binding layers. Therefore thicker binding layers (>0.8 mm) have been used to reduce this effect.

7.3.2 Electric field parameter, κ , in the uranium-sodium bicarbonate model solutions

The uranium uptake by Chelex-100 binding layer in U-NaHCO₃ model solutions as a function of the applied potential is shown in Figure 7.4. When the applied potential was 0 V, the gel electrode worked as a traditional DGT device, in which the driving force is the concentration gradient. As the applied positive potential was increased above zero, the uranium uptake increased. A linear relationship was found between the uranium uptake and the applied potential. According to the Eq. 7.7, the slope of the curve s is equal to $\frac{c_b}{\Delta g} t A \kappa$. The value of κ is $1.13 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1} \text{ V}^{-1}$. If the applied voltage was 9V, the uranium uptake of the new DGT devices was about 8 times higher than that of the

traditional DGT devices. When a negative potential (i.e., lower than 0) was applied, the uranium uptake decreased with increasing negative potential and reached zero at about -1V.

The major uranium species in these model solutions are $\text{UO}_2(\text{CO}_3)_3^{4-}$ and $\text{UO}_2(\text{CO}_3)_2^{2-}$, which are in anionic forms[5]. When a positive potential is applied to the DGT device, these anions are attracted by the electric field to the DGT device and the concentration gradient also drives the uranium species to the DGT binding layers. The flux of uranium increases with increasing applied potential. When a negative potential is applied to the DGT devices, these anions are excluded from DGT device by the electric field; however, the concentration gradient still impels these uranium species to move towards the DGT devices. The flux of uranium decreases with increasing negative potential. When the driving force of electric field is equal to that of concentration gradient, the net flux of uranium is zero.

Figure 7.4 Uranium uptake by the new DGT devices as a function of applied potential, uranium- sodium bicarbonate model solutions. Uranium concentration $100 \mu\text{g L}^{-1}$, NaHCO_3 concentration 0.01 mol L^{-1} , pH 8. Experimental time 1 hour.

7.3.3 Recovery of uranium from the new DGT device at various uranium concentrations levels

In the concentration range of $0.1\text{-}100 \mu\text{g L}^{-1}$, the uranium uptake by the new DGT device increased with increasing uranium concentration in the U- NaHCO_3 model solutions, as shown in Figure 7.5. The concentration of bulk solution c_b was calculated by using Eq. 7.8. The recovery of uranium, defined as the ratio of the calculated concentration to the initial concentration in the bulk solution, was 84%. The recovery of uranium in the

traditional DGT devices, which is defined as the percentage of DGT-labile uranium species (%L) in Chapter 5, was 70%.

Figure 7.5 Uranium uptake by the new DGT device in uranium- sodium bicarbonate model solutions. Uranium concentration 0.1, 1, 10 and 100 $\mu\text{g L}^{-1}$, NaHCO_3 0.01 mol L^{-1} , pH 8.

Black bar: Applied potential +3 V.

Grey bar: No applied potential. Experimental time 3 hours.

7.3.4 Experimental time and uranium uptake by the new DGT device

The uranium uptake by Chelex-100 binding layer in U- NaHCO_3 model solutions as a function of the experimental time is presented as Figure 7.6. As expected, the uranium uptake increased linearly with increasing experimental time. According to Eq. 7.7, the

slope of the curve, which reflects the uranium uptake rate of the new DGT device, is $\frac{c_b}{\Delta g}(D + \kappa U) \times A$. The uranium uptake rate of the new DGT device is faster than that of traditional DGT device. If the applied potential increases, the linear curve will become steeper.

Figure 7.6 Uranium uptake by the new DGT devices as a function of experimental time, in uranium- sodium bicarbonate model solutions. Uranium concentration $100 \mu\text{g L}^{-1}$, NaHCO_3 0.01 mol L^{-1} , pH 8. Applied potential +3 V. Experimental time 1-4 hours. The dashed line is the uranium uptake by traditional Chelex-100 DGT as a function of time.

7.3.5 Uranium uptake by the new DGT device in the uranium-sodium acetate buffer, at pH 4.5

The uranium uptake by Chelex-100 resin in the new DGT device in the acetic acid/acetate buffer (pH 4.5) is presented in Figure 7.7; the abbreviation Ac refers to the acetyl group. The predominant uranium species in this model solution are UO_2^{2+} and $\text{UO}_2\text{-Ac}^+$. As the applied positive potential was increased above zero, the uranium uptake decreased. When a negative potential (lower than 0) was applied, the uranium uptake increased and reached the maximum value at -1 V. However, the uranium uptake decreased as the applied negative potential was lower than -1 V.

Since the model solution was acidic, the effect of hydrogen ion on the new DGT device was probably important. The mobility of hydrogen ion (H^+) is much greater than that of other metal ions[6]. Hence, when a negative potential is applied, a large number of hydrogen ions move towards gel electrode. The uranium ions bound by Chelex-100 resin could be eluted by these hydrogen ions, resulting in decreasing uranium uptake. Hence, the new DGT device is not suitable for acidic waters.

7.3.6 Uranium uptake by the new DGT devices at high applied potential and at high ionic strength

Since most of the time the applied potential is higher than the standard reduction potential of water, the water is electrolysed during the experiment. Hydrogen gas and oxygen gas are produced on the surface of platinum electrodes and the gas-bubbles on the surface of

electrodes may interfere with the metal ion flux. As shown in Figure 7.8, when the applied potential was higher than 50V (potential applied by using Biorad PowerPac 300 power supply), the curve reach a plateau, indicating that the flux of uranium towards the new DGT devices was retarded by the gas-bubbles on the surface of the electrodes. The high applied potential may also lead to an increasing flux of major cations or anions, which can compete with the uranium ions for the binding sites on Chelex-100 resin.

Figure 7.7 Uranium uptake by the new DGT device as a function of the applied potential, uranium in acetic acid/acetate buffer (NaAc-HAc) model solutions. Uranium concentration $100 \mu\text{g L}^{-1}$, NaAc-HAc 0.01 mol L^{-1} , pH 4.5. Experimental time 1 hour

Similar results were found when the ionic strength of the test solutions was higher than 0.1 mol L^{-1} . At the above high ionic strength, the conductivity of the solutions increased and more hydrogen gas and oxygen gas were formed on the surface of electrode. The gas-bubbles and the flux of cations or anion might probably even hinder the adsorption of uranium on the Chelex-100 resin.

Figure 7.8 Uranium uptake by the new DGT device as a function of the applied potential, uranium- sodium bicarbonate model solutions. Uranium concentration $100 \mu\text{g L}^{-1}$, NaHCO_3 0.01 mol L^{-1} , pH 8. Experimental time 1 hour. Applied potential 0-200 V.

7.3.7 Field applications

A rechargeable battery (MotoMaster Eliminator Power Box, 400 W/ 600 A) and a DC power supply (HP Harrison 6205B Dural DC power supply) were used in field studies and the new DGT device was modified for field applications. The gel electrodes were set up as early described (Figure 7.1). Three gel electrodes were placed in the holes (A, B and C) of the cap of VA stand, and one gel electrode, which was placed in the hole D as a reference without applying potential (Figure 7.9). The platinum auxiliary electrode was placed in the middle as presented in Figure 7.9. The device was then inserted in a foam buoy and connected to the power supply (Figure 7.10).

On August 25, 2007, the new DGT device was deployed in Rideau River and the applied potential was set at +10 V on gel electrodes. After 3 hours deployment, the device was taken out of the river and the DGT binding layers were eluted using 20% HNO₃. the uranium concentratin in elution was determined using KPA as described in Chapter 2.

The device was calibrated using uranium model solutions containing uranium 10-200 µg L⁻¹ and sodium bicarbonate 0.01 mol L⁻¹, as shown in Figure 7.11. According to the Eq. 7.7, the slope of the linear calibration curve M versus C_b is $(D + \kappa U) \times t \times A / \Delta g$. As the slope of the calibration curve is known, the electrode parameter κ can be obtained. The value of κ is $4.13 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1} \text{ V}^{-1}$.

Figure 7.9 New DGT device Assembly for field work (step 1)

Figure 7.10 New DGT device Assembly for field work (step 2)

The total uranium concentration in Rideau River was $0.9 \mu\text{g L}^{-1}$, determined by KPA. The pH of Rideau River water is about 8. The concentration measured by new DGT device was 86.8% of total uranium concentration, according to Eq. 7.8, which is higher than the percentage of concentration measured by traditional DGT device in field studies (about 60%) [2, 3] .

Figure 7.11 Calibration curve of New DGT device for field study in model solutions. Uranium 10-200 $\mu\text{g L}^{-1}$ and sodium bicarbonate 0.01 mol L^{-1} . Applied potential +9V. Experimental time 30 min.

7.4 Conclusions

The new DGT device is suitable for pre-concentrating uranium and investigating uranium speciation in alkaline waters. It has promise of being used for studying metal speciation and pre-concentration of other trace metal ions.

Advantages of the new method

1. The metal flux is higher than in the traditional DGT device. The mass of metal accumulated in the DGT binding layer increases significantly.
2. The metal flux can be easily controlled by adjusting the applied voltage, the higher voltage the faster the metal transport.
3. Metal species may be differentiated in the applied electric field by their different electric charges. This property is especially important for uranium, because uranium species in freshwater systems have both negative and positive charges.

7.5 References

1. Durrance, E.M. (1986). Radioactivity in geology: principles and applications (Chichester [West Sussex]New York: E. Horwood ;Halsted Press).
2. Li, W., Li, C., Zhao, J., and Cornett, R.J. (2007). Diffusive gradients in thin films technique for uranium measurements in river water. *Analytica Chimica Acta* 592, 106-113.
3. Li, W., Zhao, J., Li, C., Kiser, S., and Cornett, R.J. (2006). Speciation measurements of uranium in alkaline waters using diffusive gradients in thin films technique. *Analytica Chimica Acta* 575, 274-280.
4. Koryta, J.r., Dvorák, J.r., and Kavan, L. (1993). Principles of electrochemistry. In *Principles of electrochemistry*, 2nd Edition. (Chichester ; New York: Wiley), p. 115.
5. Markich, S.J. (2002). Uranium speciation and bioavailability in aquatic systems: An overview. *TheScientificWorld* [online computer file] 2, 707-729.
6. Atkins, P.W. (1998). Physical chemistry. In *Physical chemistry*, 6th Edition. (New York: W.H. Freeman), p. 727.

Chapter 8

Field studies

8.1 Introduction

DGT represents a reliable *in-situ* sampling tool and a speciation technique, which offers promise of linking uranium species to their bioavailability and toxicity. However, the published literature does not report results of long-term field studies on uranium speciation in surface freshwaters using DGT. The objective of the work in this Chapter is to fill the above gap in our knowledge so as to confer predictive capability for bioavailability and ecotoxicity.

8.2 Experimental

8.2.1 Deployment site

The DGT deployment site is located at a spot a short way upstream of the Hartwell locks in the Rideau Canal beside Carleton University campus in Ottawa (Figure 8.1).

8.2.2 Experimental procedures

The whole field work time was from August 1, 2007 to October 18, 2007. Every week, 14 DGT devices (five Chelex-100, three DE81, three P81 and three polymer-A binding layers) were deployed at the sampling site. These DGT devices were retrieved from the sampling site after 2 weeks deployment. The uranium accumulated by the binding layers was eluted with 20% (v/v) HNO₃ and the uranium concentration was determined by KPA, as described in Chapter 2. The temperature of the water was recorded and some water samples were collected. The pH and conductivity were measured by an Accumet 20 pH/conductivity meter (Fisher Scientific). The Dissolved Organic Carbon (DOC) and Inorganic Carbon (IC) concentration of the water samples was determined using a

Shimadzu Total Organic Carbon Analyzer (TOC-VCPH). The major cations (Ca and Mg) were measured using Perkin-Elmer AA 600 GFAAS. The total uranium concentration and some trace metal concentrations were determined using Perkin-Elmer Elan DRC-e ICP-MS.

8.2.3 QA/QC

Quality control for uranium and other trace metal analyses in natural surface waters included periodical analysis of Certified Reference Materials NIST 1640 and SLRS-4 (natural waters) using ICP-MS. All the recovery values reported in Table 8.1 are calculated as a percentage of the certified values. The recoveries for all the elements are within 90-110% except Al, Cr and As for NIST 1640 and Al, Mn and Zn for SLRS-4. All measurements were done in triplicate. Blanks and calibration standards were re-determined every two hours to monitor the instrument performance.

When DGT field samplers were deployed, at least three DGT field blank samplers were prepared following the same procedure. The field blanks were then deployed in ultrapure water for the same deployment time as DGT field samplers.

Table 8.1 Recovery of natural water CRMs

	SLRS-4			NIST 1640		
	Measured concentration ($\mu\text{g L}^{-1}$)	Certified concentration ($\mu\text{g L}^{-1}$)	Recovery (%)	Measured Concentration ($\mu\text{g L}^{-1}$)	Certified concentration ($\mu\text{g L}^{-1}$)	Recovery (%)
Al	42±1	54±4	78.6	30.0±0.2	52.0±1.5	57.9
Cr	0.30±0.03	0.33±0.02	90.9	22.1±0.3	38.6±1.6	57.2
Mn	2.48±0.06	3.37±0.18	73.6	121.6±1.3	121.5±1.1	100.1
Ni	0.62±0.02	0.67±0.08	91.8	26.2±0.8	27.4±0.8	95.5
Cu	1.71±0.04	1.81±0.08	94.2	81.8±3.2	85.2±1.2	96.0
Zn	1.14±0.14	0.93±0.10	122.0	57.0±0.8	53.2±1.1	107.1
As	0.63±0.02	0.68±0.06	92.8	20.86±0.25	26.67±0.41	78.2
Cd	0.013±0.004	0.012±0.002	108.3	21.76±0.42	22.79±0.96	95.5
Sb	0.251±0.007	0.23±0.04	109.1	13.09±0.09	13.79±0.42	94.9
Pb	0.084±0.007	0.086±0.007	97.7	26.05±0.23	27.89±0.14	93.4
U	0.049±0.002	0.050±0.003	98.0	0.78±0.01	N/A	N/A

8.3 Results and discussion

8.3.1 Speciation parameters

The speciation parameters (temperature, pH, conductivity, TOC and IC) in the Rideau Canal water are presented in Figures 8.2-8.5. Concentrations of some trace metal are presented in Table 8.2. Concentrations of major cations, Ca and Mg, are presented in Table 8.3. Cu concentrations were changed very much and in some samples were at very high level probably because of the contamination by the boats in the sampling area.

During the deployment period, the temperature of the Rideau Canal water samples decreased from 28.7°C to about 20°C; the pH varied in the range of 7.8-8.8, indicating Rideau Canal water was slightly alkaline. The conductivity of the Rideau Canal water samples was 577-722 $\mu\text{S cm}^{-1}$. The ionic strength of Rideau Canal water samples can be calculated from electrical conductivity using the following empirical relationship [1]:

$$\text{IS} = 0.014 \times \text{EC} - 4 \times 10^{-4} \quad (8.1)$$

where IS is ionic strength (mol L^{-1}), EC is electrical conductivity (mS cm^{-1}). The concentration of the dissolved organic carbon (DOC) and the inorganic carbon (IC) of the Rideau Canal water samples are presented in Figure 8.4. The DOC concentration was within 9-14 mg L^{-1} , whereas the IC concentration was in the range of 25-30 mg L^{-1} .

Figure 8.2 Temperature in the Rideau Canal water measured during deployment period.

Figure 8.3 pH in the Rideau Canal water measured during deployment period.

Figure 8.4 Electrical conductivity in the Rideau Canal water measured during deployment period.

Figure 8.5 TOC and IC in the Rideau Canal water measured during deployment period. ◆: IC; ●: TOC

Table 8.2 Trace metal concentrations in the Rideau Canal water samples during the DGT deployment period using ICP-MS.

Date	Metal concentration			
	Al ($\mu\text{g L}^{-1}$)	Cr ($\mu\text{g L}^{-1}$)	Mn ($\mu\text{g L}^{-1}$)	Ni ($\mu\text{g L}^{-1}$)
1-Aug-07	2.07 $\pm$ 0.17	6.23 $\pm$ 0.13	0.24 $\pm$ 0.011	0.74 $\pm$ 0.02
8-Aug-07	8.83 $\pm$ 0.33	1.84 $\pm$ 0.15	0.10 $\pm$ 0.005	0.55 $\pm$ 0.03
14-Aug-07	10.98 $\pm$ 0.16	2.15 $\pm$ 0.02	0.097 $\pm$ 0.002	0.32 $\pm$ 0.03
21-Aug-07	10.67 $\pm$ 0.17	2.17 $\pm$ 0.14	0.13 $\pm$ 0.008	0.39 $\pm$ 0.05
28-Aug-07	10.73 $\pm$ 0.30	2.27 $\pm$ 0.13	0.07 $\pm$ 0.006	0.42 $\pm$ 0.04
4-Sep-07	10.99 $\pm$ 0.10	2.54 $\pm$ 0.07	0.53 $\pm$ 0.013	0.38 $\pm$ 0.02
12-Sep-07	30.19 $\pm$ 0.58	2.23 $\pm$ 0.09	0.50 $\pm$ 0.019	0.93 $\pm$ 0.01
19-Sep-07	10.54 $\pm$ 0.12	2.37 $\pm$ 0.09	0.17 $\pm$ 0.013	0.74 $\pm$ 0.04
26-Sep-07	15.04 $\pm$ 0.13	2.20 $\pm$ 0.07	0.12 $\pm$ 0.004	1.74 $\pm$ 0.04
3-Oct-07	18.79 $\pm$ 0.17	15.3 $\pm$ 1.77	2.00 $\pm$ 0.053	0.64 $\pm$ 0.02
10-Oct-07	11.92 $\pm$ 0.17	2.39 $\pm$ 0.01	0.36 $\pm$ 0.005	0.56 $\pm$ 0.02
18-Oct-07	12.46 $\pm$ 0.22	2.55 $\pm$ 0.08	0.68 $\pm$ 0.017	0.53 $\pm$ 0.06

Table 8.2 Trace metal concentrations in the Rideau Canal water samples during the DGT deployment period using ICP-MS. (continued)

Date	Metal concentration			
	Cu ($\mu\text{g L}^{-1}$)	Zn ($\mu\text{g L}^{-1}$)	As ($\mu\text{g L}^{-1}$)	Sn ($\mu\text{g L}^{-1}$)
1-Aug-07	1.74 $\pm$ 0.06	7.90 $\pm$ 0.84	1.08 $\pm$ 0.03	0.07 $\pm$ 0.012
8-Aug-07	1.30 $\pm$ 0.03	6.90 $\pm$ 0.18	0.63 $\pm$ 0.03	0.02 $\pm$ 0.006
14-Aug-07	76.96 $\pm$ 0.60	8.32 $\pm$ 0.19	0.33 $\pm$ 0.01	3.18 $\pm$ 0.017
21-Aug-07	0.83 $\pm$ 0.01	8.10 $\pm$ 0.18	0.75 $\pm$ 0.04	0.01 $\pm$ 0.001
28-Aug-07	1.01 $\pm$ 0.03	7.04 $\pm$ 0.14	0.69 $\pm$ 0.03	0.01 $\pm$ 0.003
4-Sep-07	64.08 $\pm$ 1.74	5.28 $\pm$ 0.27	0.70 $\pm$ 0.04	1.99 $\pm$ 0.024
12-Sep-07	2.34 $\pm$ 0.04	33.85 $\pm$ 0.49	0.54 $\pm$ 0.01	0.04 $\pm$ 0.001
19-Sep-07	5.51 $\pm$ 0.18	8.81 $\pm$ 0.29	0.59 $\pm$ 0.02	0.11 $\pm$ 0.007
26-Sep-07	2.28 $\pm$ 0.06	7.45 $\pm$ 0.21	0.62 $\pm$ 0.02	0.05 $\pm$ 0.006
3-Oct-07	109.17 $\pm$ 1.91	9.51 $\pm$ 0.20	0.58 $\pm$ 0.03	4.38 $\pm$ 0.056
10-Oct-07	2.79 $\pm$ 0.07	6.16 $\pm$ 0.12	0.44 $\pm$ 0.02	0.07 $\pm$ 0.004
18-Oct-07	12.67 $\pm$ 0.21	16.72 $\pm$ 0.17	0.55 $\pm$ 0.02	0.45 $\pm$ 0.013

Table 8.3 Concentration of calcium and magnesium in the Rideau Canal water samples during the DGT deployment period.

Date	Concentrations*	
	Ca (mg L ⁻¹)	Mg (mg L ⁻¹)
8-Aug-07	9.3	2.3
14-Aug-07	17.1	2.3
21-Aug-07	18.8	2.2
28-Aug-07	8.3	2.3
4-Sep-07	13.5	2.3
12-Sep-07	12.0	2.3
19-Sep-07	23.6	2.2
26-Sep-07	36.5	2.3
3-Oct-07	5.6	2.2
10-Oct-07	29.7	2.2
18-Oct-07	49.1	2.2

*The standard deviation of Ca measurements was less than about 5%; while that of Mg measurements was less than 10%.

8.3.2 Uranium uptake by DGT binding layers

The total uranium concentration in the Rideau Canal water varied from 0.4 to 1.2 $\mu\text{g L}^{-1}$ during the whole period of the field study (Figure 8.6). Two peaks are presented in Figure 8.6, on August 8, 2007 and October 10, 2007.

The effective uranium concentrations determined by different DGT binding layers, as shown in Figures 8.7- 8.10, were calculated from uranium uptake (Table 8.4) using Eq. 5.8. The effective uranium concentrations measured by Chelex-100 and DE81 showed a similar trend, with two peaks on August 28, 2007 and October 11, 2007. The trend probably corresponded to the variation of total uranium concentration in the Rideau Canal water during the deployment period. The effective uranium concentration measured by DE81 was higher than that measured by Chelex-100, indicating that in the Rideau Canal water the apparent lability factor ϕ_{U_i} of uranium species for DE81 is higher than that for Chelex-100, as discussed in Chapter 5. The effective concentration obtained by P81 DGT decreased during the deployment period, indicating the cationic forms of the uranium species decreased. The effective uranium concentration of polymer-A DGT was higher than that of other DGT binding layers, indicating the polymer-A had a greater binding affinity for the uranium species. However, the polymer-A DGT was not affected by the variation of the total uranium concentration in the Rideau Canal water.

The variation of total uranium concentration in the Rideau Canal water might result from the uranium input from storm runoff in the upriver area, which directly affected the uranium uptake by Chelex-100 and DE81 DGT. The uranium uptake by DE81 DGT

reflected the anionic forms of uranium species, which had a greater fraction of the total uranium species and showed a similar trend as the total uranium concentration. The large standard deviation of some DGT samples is probably due to the impact of environmental condition on the DGT devices in field deployments, such as the bio-fouling effect.

Figure 8. 6 Uranium concentration in the Rideau Canal water samples.

Table 8.4 Uranium uptake by DGT in the Rideau Canal water samples during the DGT deployment period.

Date	Uranium uptake by DGT (µg)							
	Chelex-100		DE81		P81		Polymer-A	
14-Aug-07	0.0014	±0.0008	0.0056	±0.0008	0.0037	±0.0002	0.0223	±0.0054
21-Aug-07	0.0027	±0.0006	0.0090	±0.0041	0.0029	±0.0007	0.0138	±0.0029
28-Aug-07	0.0028	±0.0005	0.0066	±0.0023	0.0016	±0.0001	0.0056	±0.0002
04-Sep-07	0.0043	±0.0019	0.0104	±0.0027	0.0026	±0.0004	0.0239	±0.0036
12-Sep-07	0.0009	±0.0005	0.0098	±0.0017	0.0025	±0.0002	0.0174	±0.0063
19-Sep-07	0.0019	±0.0011	0.0116	±0.0035	0.0016	±0.0012	0.0159	±0.0015
03-Oct-07	0.0035	±0.0021	0.0122	±0.0038	0.0017	±0.0006	0.0153	±0.0025
10-Oct-07	0.0115	±0.0023	0.0153	±0.0030	0.0012	±0.0002	0.0160	±0.0025
18-Oct-07	0.0075	±0.0021	0.0076	±0.0027	0.0019	±0.0001	0.0099	±0.0010

Figure 8. 7 Effective uranium concentration in the Rideau Canal water measured by Chelex-100 DGT.

Figure 8. 8 Effective uranium concentration in the Rideau Canal water measured by DE81 DGT.

Figure 8. 9 Effective uranium concentration in the Rideau Canal water measured by P81 DGT.

Figure 8. 10 Effective uranium concentration in the Rideau Canal water measured by Polymer-A DGT.

8.8.3 Correlation analysis

The percentage of DGT-labile uranium species (%L) in Rideau Canal were calculated using Eq. 5.13, and are presented in Table 8.5 and Figure 8.11. %L and speciation parameters data were analyzed using SigmaStat for Windows Version 2.03. The correlation coefficient values are presented in the Table 8.6. Although the correlation does not infer a causal relationship, it gives us useful information about the relationship between the %L and the speciation parameters. The higher correlation coefficient (0.5 to 1 or -0.5 to -1) indicates more linear relationship between the two variables. %L for Chelex-100 DGT has a negative correlation with the EC (ionic strength) and with IC (inorganic carbonate) probably because the competition between major ions with uranium species for binding with Chelex-100 resin layer, as discussed in Chapter 4 and 5. A significant positive correlation between %L for Chelex-100 DGT with the concentration of calcium has been found, indicating that calcium may increase the DGT-labile fractions of uranium by competing with uranium for binding with dissolved organic carbon and forming U-Ca-carbonate species, which may play a very important role in uranium speciation[2, 3]. %L for P81 DGT has a significant negative correlation with total uranium concentration, indicating that the fraction of cationic forms in uranium species decreases with increasing total uranium concentration in the Rideau Canal water. Other correlations have been found not significant, even though some of them show high correlation coefficient values.

The toxicity and bioavailability of uranium are dependent on speciation parameters such as hardness and alkalinity[4-6] and DOC[7, 8] in surface freshwaters. Practically,

laboratory-based microorganism culture has been used for testing the uranium toxicity. The culture medium contains nutrients and buffers, and the uranium concentrations are set at mg L^{-1} levels, which are about 1,000 times higher than the uranium concentrations in real uncontaminated freshwater samples [6, 8, 9]. Therefore the distribution of uranium species in culture medium is not able to represent the uranium speciation in natural surface freshwaters.

Although the uranium concentrations in surface freshwaters are at very low levels, the chronic toxicity of uranium still affects the organism, especially the animals on the top of food chain, because of the bioaccumulation, which has been studied by other workers [10, 11]. Barillet et al.[12] have reported that the bioconcentration (bioaccumulation) factors of uranium for zebrafish (*Danio rerio*) were time dependent and ranged from 31 (3 days) to 149 (20 days). The field-based technique, DGT, simulates the process of metal binding by microorganism and provides a way to determine the uranium labile species, which can be used to evaluate the bioavailability of uranium and hence the toxicity. In this study various DGT binding layers were used to assess the impacts of different uranium labile species. However, some other factors can also affect the accuracy of the data. For example, bio-fouling[13], which is an undesirable accumulation of microorganisms on the surface of DGT in field deployment, may result in the blockage of the sampling window of DGT and reduce the uranium uptake by the DGT binding layers.

Table 8.5 Percentage of DGT-labile uranium species (%L) calculated by various DGT binding layers in the Rideau Canal water.

Date	Percentage of DGT-labile uranium species (%L)*			
	Chelex-100	DE81	P81	Polymer-A
14-Aug-07	1.1%	4.3%	2.9%	17.2%
21-Aug-07	1.7%	5.7%	1.8%	8.7%
28-Aug-07	6.0%	14.1%	3.4%	12.0%
4-Sep-07	5.1%	12.2%	3.1%	28.2%
12-Sep-07	1.2%	13.1%	3.4%	23.3%
19-Sep-07	2.6%	16.1%	2.2%	22.0%
3-Oct-07	5.3%	18.3%	2.6%	22.9%
10-Oct-07	13.7%	18.3%	1.5%	19.1%
18-Oct-07	13.1%	13.3%	3.3%	17.2%

*These values were calculated theoretically and the standard deviation was not shown.

Uranium speciation in aqueous system is so complicated that it is impossible to use one or a few factors to explain the distribution of uranium labile species that is available to biota. Since natural waters are open systems, the speciation parameters change all the time. Limited data (once a week) may not reflect the whole picture of the variation of speciation parameters during the DGT deployment period (about two months). Even though the results may not explain the exact uranium speciation and the effects of all the speciation parameters on the DGT-labile species, this study has presented a method to evaluate the distribution of uranium species and its bioavailability in surface freshwaters using DGT.

Figure 8. 11 Percentage of DGT-labile uranium species (%L) during the deployment period.

■: Chelex-100; △: P81; □: DE81; ▲: Polymer-A

Table 8.6 Correlation coefficients of percentage of DGT-labile uranium species (%L) and speciation parameters in Rideau Canal (total uranium concentration, temperature, pH, electrical conductivity, TOC, IC, calcium and magnesium concentrations.)

DGT binding layer	Correlation coefficient						
	U(total)	T	pH	EC	TOC	IC	Ca Mg
Chelex-100	0.522	-0.331	-0.206	-0.810**	0.408	-0.565	0.667* -0.209
DE81	0.33	-0.594	0.452	-0.552	0.211	-0.386	0.04 -0.182
P81	-0.736*	0.435	0.189	0.183	-0.513	-0.245	-0.123 0.582
Polymer-A	-0.04	-0.246	0.421	0.015	-0.499	-0.439	-0.142 0.181

** Correlation is significant at the 0.01 level (2-tailed).

* Correlation is significant at the 0.05 level (2-tailed).

These values were calculated theoretically and the standard deviation was not shown.

8.4 References

1. Hassan, N.M., Murimboh, J.D., Sekaly, A.L.R., Mandal, R., Chakrabarti, C.L., and Gregoire, D.C. (2006). Cascade ultrafiltration and competing ligand exchange for kinetic speciation of aluminum, iron, and nickel in fresh water. *Analytical and Bioanalytical Chemistry* 384, 1558-1566.
2. Bernhard, G., Geipel, G., Reich, T., Brendler, V., Amayri, S., and Nitsche, H. (2001). Uranyl(VI) carbonate complex formation: validation of the $\text{Ca}_2\text{UO}_2(\text{CO}_3)_3(\text{aq.})$ species. *Radiochimica Acta* 89, 511-518.
3. Wang, Z., Zachara, J.M., Yantasee, W., Gassman, P.L., Liu, C., and Joly, A.G. (2004). Cryogenic Laser Induced Fluorescence Characterization of U(VI) in Hanford Vadose Zone Pore Waters. *Environmental Science and Technology* 38, 5591-5597.
4. Sheppard Steve, C., Sheppard Marsha, I., Gallerand, M.-O., and Sanipelli, B. (2005). Derivation of ecotoxicity thresholds for uranium. *Journal of Environmental Radioactivity* 79, 55-83.
5. Poston, T.M., Hanf, R.W., Jr., and Simmons, M.A. (1984). Toxicity of uranium to *Daphnia magna*. *Water, Air, and Soil Pollution* 22, 289-298.
6. Zeman, F.A., Gilbin, R., Alonzo, F., Lecomte-Pradines, C., Garnier-Laplace, J., and Aliaume, C. (2008). Effects of waterborne uranium on survival, growth, reproduction and physiological processes of the freshwater cladoceran *Daphnia magna*. *Aquatic Toxicology* 86, 370-378.
7. Markich, S.J. (2002). Uranium speciation and bioavailability in aquatic systems: An overview. *TheScientificWorld* [online computer file] 2, 707-729.
8. Hogan, A.C., van Dam, R.A., Markich, S.J., and Camilleri, C. (2005). Chronic toxicity of uranium to a tropical green alga (*Chlorella* sp.) in natural waters and the influence of dissolved organic carbon. *Aquatic Toxicology* 75, 343-353.
9. Fortin, C., Dutel, L., and Garnier-Laplace, J. (2004). Uranium complexation and uptake by a green alga in relation to chemical speciation: the importance of the free uranyl ion. *Environmental toxicology and chemistry / SETAC* 23, 974-981.
10. DeForest, D.K., Brix, K.V., and Adams, W.J. (2007). Assessing metal bioaccumulation in aquatic environments: The inverse relationship between bioaccumulation factors, trophic transfer factors and exposure concentration. *Aquatic Toxicology* 84, 236-246.
11. Goodyear, K.L., and McNeill, S. (1999). Bioaccumulation of heavy metals by aquatic macro-invertebrates of different feeding guilds: a review. *Science of the Total Environment* 229, 1-19.
12. Barillet, S., Adam, C., Palluel, O., and Devaux, A. (2007). Bioaccumulation, oxidative stress, and neurotoxicity in *Danio rerio* exposed to different isotopic compositions of uranium. *Environmental Toxicology and Chemistry* 26, 497-505.
13. Webb, J.A., and Keough, M.J. (2002). Measurement of environmental trace-metal levels with transplanted mussels and diffusive gradients in thin films (DGT): a comparison of techniques. *Marine Pollution Bulletin* 44, 222-229.

Chapter 9

Conclusions

The study of metal speciation and bioavailability is based on three hypotheses:

1. The bioavailability and toxicity of a metal are dependent on metal speciation.
2. The distribution of metal species can be measured by speciation techniques.
3. The bioavailability and toxicity of a metal are correlated to the species determined by the speciation techniques.

The first hypothesis has been validated by many researchers and has now become the basic premise of the study of the metal speciation. The objective of this thesis is to test the second hypothesis, that a speciation technique, Diffusive Gradients in Thin Films (DGT), can be used to identify and qualify the factors that control the speciation of uranium in surface freshwaters. Additional studies are required for testing whether or not DGT can provide an insight into any possible linkages between uranium speciation and their bioavailability and ecotoxicity in surface freshwaters.

The approach used in the research work is to:

1. Study the performance of several diffusive layers and binding layers to determine their suitability for uranium speciation
2. Present a theory to interpret the DGT data on the uranium speciation in surface freshwaters
3. Apply the DGT device and the above theory to *in-situ* experiment in surface freshwaters

Since DGT is a technique based on diffusion coupled with chemical reaction, the diffusion and the binding properties of DGT are of importance. The DGT diffusive layer

and the binding layers were characterized in model solutions. The diffusion coefficients of uranium in the polyacryamide gel varied with different pH and complexing agents in model solutions. The four DGT binding layers: Chelex-100 ion-exchange resin, DE81 ion-exchange filter membrane, P81 ion-exchange filter membrane and a new polymer, Poly (salicylaldoxime-3, 5-diyl (N, N'-dimethylethylenediamine N, N'-bismethylene)), were tested at different pH, ionic strength and in synthetic fresh water samples and were found to be suitable for deployment in natural surface freshwaters.

To gain an insight into the uranium speciation in natural waters, the effective uranium concentration c_{Ueff} and the percentage of DGT-labile uranium species % L were applied to interpret the DGT results. The apparent lability factor ϕ_{Ui} and the percentage distribution of uranium species θ_{Ui} were used to evaluate the DGT-lability of different uranium species. A reference model solution was used so that all the results can be compared. Strong complexing agent reduced the percentage of DGT-labile uranium species, whereas competition between copper and uranium for binding with HS increased the percentage of DGT-labile uranium species. The percentage of uranium DGT-labile species increased with increasing ionic strength in model solutions, indicating that ionic strength might affect the binding of uranium with humic substances. At higher pH, the percentage of DGT-labile uranium species increased probably because of the formation of inorganic uranium species. The percentage distribution of $UO_2(CO_3)_2^{2-}$ had the same trend as the percentage of DGT-labile uranium species in U-NaHCO₃-HA model solutions, indicating it had a higher apparent lability factor value, ϕ . There is some impact of atmospheric CO₂

on the uranium speciation and the uranium uptake by DGT in U-HA ($\text{HA} < 0.6 \text{ mg L}^{-1}$) and U-FA ($\text{FA} < 1 \text{ mg L}^{-1}$) model solutions.

The competitive Ligand Exchange Method (CLEM) was used to obtain the lability factor, α , which is the key parameter for evaluating the lability of the DGT-labile species, in U-HA systems. Since humic acid (HA) is a chemically and physically heterogeneous complexing agent, the lability factor, α , is the percentage of U-HA species that can react with Chelex-100 resin binding layer during an experiment. The uranium species were characterized either as a “labile” or a “non-labile” uranium complex depending on the dissociation rate coefficients of the complexes. With increasing HA concentrations, the labile fraction of uranium species decreased. When HA concentration is 0.2 mg L^{-1} , in presence of atmospheric CO_2 , the U-carbonate species can be considered as labile fraction and cannot be distinguished from other labile species such as U-hydroxide and U binding with the weak binding sites of HA. The labile component in natural surface water samples was most probably uranium-carbonate species, whereas the non-labile component was the uranium bound to the strong binding sites of DOC. The DGT binding process can follow both Adjunctive and Disjunctive Pathways. CLEM can provide the information on the dissociation coefficient of a metal-ligand complex, if the process follows Disjunctive Pathway. However, in the case of Adjunctive Pathway, CLEM is not able to provide the dissociation rate coefficients of the metal complexes.

The development of an improved version of DGT was tested using an applied electrical potential to accelerate mass transport. This method was found to be suitable for alkaline

waters to overcome the limitation for traditional DGT devices (low uranium uptake rate and long deployment time).

The DGT devices were also applied to a long-term field study to evaluate its practicality in routine operations. Various DGT binding layers was used to assess the impacts of speciation parameters on the distribution of uranium species by correlation studies. A significant positive correlation between the Chelex-100 DGT labile species and the concentration of calcium was found, indicating that calcium may increase the DGT-labile fractions of uranium.

ACHIEVEMENTS AND ENVIRONMENTAL SIGNIFICANCE OF THIS THESIS

- a. The major achievement of this work is to demonstrate that the recently-invented technique, Diffusive Gradients in Thin Films (DGT) is an effective technique for the study of uranium speciation in natural surface freshwaters.
- b. A theory on DGT labile species is presented and the terms ‘effective concentration’ and ‘uranium DGT-labile species’ are “operationally-defined” and then used to interpret the uranium speciation in surface freshwaters.
- c. The development of DGT device using an applied electrical potential is proven to accelerate mass transport, and hence to improve the measurement of uranium species in surface freshwaters.

Appendix A -Impact of atmospheric CO₂ on the uranium speciation

The objective of this work is to investigate the impact of atmospheric CO₂ on the uranium speciation in the model solutions used in this thesis work.

Model solutions used in the thesis

The model solutions used in the thesis work include uranium-humic acid (U-HA), uranium-fulvic acid (U-FA), uranium-sodium bicarbonate (U-NaHCO₃), uranium-sodium carbonate (U-Na₂CO₃) and uranium-sodium nitrate (U-NaNO₃). U-HA and U-FA model solutions were equilibrated before experiment in closed bottles for 24-48 hours. Synthetic river water and natural water samples, which contained CO₃²⁻ and were well equilibrated with atmosphere before experiment, have not been discussed in this report.

The model solutions used to determine the uranium diffusion coefficients were prepared in 1000 mL HDPE containers (Chapter 3). Those model solutions were open to atmosphere and the experimental time was 2 hours for U-NaNO₃ model solutions and several days for U-HA model solutions.

The model solutions used to determine the uranium uptake by DGT binding layers (Chapter 4) were prepared in 250 mL or 500 mL HDPE bottles. Those bottles were capped during the experiment; the experimental time was about 24 hours.

In diffusive gradients in thin films (DGT) experiments (Chapter 5), the model solutions were prepared in 2.2 L Teflon containers. The containers were capped during the experiment and the typical deployment time was from 5 to 24 hours.

The model solutions used in competitive ligand exchange (CLEM) experiments were prepared in 500 mL Teflon containers (Chapter 6). The containers were open to atmosphere and the experimental time was about 2 hours.

As discussed earlier, the model solutions might not be at equilibrium during the experiment. Also, the bottles were not entirely airtight. Therefore, some more experiments need to be done to investigate the impact of atmospheric CO₂ on those model solutions.

Experimental

All sample solutions were prepared with deionized water of resistivity of 18.2 MΩ-cm, obtained direct from a NANOpure DIamond Ultrapure Water System (Barnstead, USA). Humic acid was supplied by Dr. Les Evans (University of Guelph, Guelph, Ontario, Canada). Fulvic acid solution was prepared using Suwannee River Fulvic Acid, obtained from International Humic Substances Society (IHSS). Nitric acid (Optima, Fisher Scientific) and sodium hydroxide (Caledon Laboratories LTD) were used to adjust the pH.

Six solutions were prepared as follows:

A: 1000 ml ultra pure water, closed

B: 1000 ml ultra pure water, open to atmosphere

C: 500 ml, containing FA 2 mg L⁻¹, uranium 1 mg L⁻¹, open to atmosphere, pH 7

D: 500 ml, containing HA 2 mg L⁻¹, uranium 1 mg L⁻¹, open to atmosphere, pH 7

E: 500 ml, containing NaNO₃ 0.01 mol L⁻¹, uranium 1 mg L⁻¹, closed, pH 9

F: 500 ml, containing NaNO₃ 0.01 mol L⁻¹, uranium 1 mg L⁻¹, open to atmosphere, pH 9

The six solutions were then placed on a Water-Bath Shaker (Model C76 Water-Bath Shaker, New Brunswick Scientific) and the temperature was set at 25°C. The experimental time was about four days. The inorganic carbon (IC) concentration in those solutions was determined using TOC Analyzer (Shimadzu TOV-V_{CPH}).

Results and discussion

Carbonate concentration

The carbonate (CO₃²⁻) in model solutions could be from ultra pure water, NaOH, which was used to adjust pH, other reagents and CO₂ in atmosphere. As presented in Table 1, the inorganic carbon (IC) in the six solutions was at very low levels during the experiment. For simplifying the discussion, the inorganic carbon species in all model solutions have been considered as CO₃²⁻, which can form uranium-carbonate species in model solutions. The CO₃²⁻ concentrations as function of time are shown in Figure 1.

The carbonate ion concentration in all the samples was lower than 2 mg L⁻¹ CO₃²⁻ during about four days experiment. The ultra pure water samples (sample A and B) did not

contain carbonate when the experiment started. Other samples contained about 0.5 mg L^{-1} carbonate at the beginning, which was probably from reagents, such as NaOH. As expected, the carbonate concentration in solution F was higher than that in other samples, because of the high pH and its exposure to the atmosphere. The carbonate concentration in solution F increased faster than that in other samples in the first 10 hours. The increase of carbonate in sample E was probably due to the inleakage of atmospheric CO_2 into the bottle when the solution sample was collected. There was no significant increase of carbonate in samples A, B, C and D, indicating the absorption of CO_2 in those systems was at very low levels. Since the detection limit of IC is about $0.1 \text{ mg L}^{-1} \text{ C}$ ($0.5 \text{ mg L}^{-1} \text{ CO}_3^{2-}$), small variation in the carbonate concentration in those samples may not be detected.

Table 1 Inorganic carbon concentration in model solutions.
A: 1000 ml ultra pure water, closed;
B: 1000 ml ultra pure water, open to the atmosphere;
C: 500 ml, containing FA 2 mg L⁻¹, uranium 1 mg L⁻¹, open to the atmosphere, pH 7;
D: 500, containing ml HA 2 mg L⁻¹, uranium 1 mg L⁻¹, open to the atmosphere, pH 7;
E: 500 ml, containing NaNO₃ 0.01 mol L⁻¹, uranium 1 mg L⁻¹, closed, pH 9;
F: 500 ml, containing NaNO₃ 0.01 mol L⁻¹, uranium 1 mg L⁻¹, open to the atmosphere, pH 9

Experimental time (hour)	Inorganic Carbon* Concentration (mg L ⁻¹ C)									
	0	3	10	24	49	72	92			
A	Less than 0.01	0.03 ±0.004	0.01 ±0.002	0.02 ±0.003	0.04 ±0.011	0.08 ±0.001	0.07 ±0.003			
B	Less than 0.01	0.05 ±0.002	0.02 ±0.001	0.04 ±0.005	0.02 ±0.007	0.04 ±0.003	0.08 ±0.010			
C	0.05 ±0.001	0.07 ±0.008	0.12 ±0.002	0.07 ±0.002	0.09 ±0.000	0.09 ±0.001	0.18 ±0.003			
D	0.16 ±0.004	0.13 ±0.006	0.09 ±0.009	0.09 ±0.003	0.14 ±0.065	0.11 ±0.007	0.13 ±0.001			
E	0.11 ±0.011	0.17 ±0.001	0.12 ±0.004	0.14 ±0.004	0.17 ±0.007	0.21 ±0.005	0.31 ±0.011			
F	0.10 ±0.004	0.19 ±0.003	0.29 ±0.005	0.28 ±0.005	0.33 ±0.002	0.34 ±0.007	0.36 ±0.001			

*The detection limit of IC is about 0.1 mg L⁻¹ C.

Figure 1 Carbonate concentration in model solutions as function of experimental time.

▲: sample A; △: sample B; ■: sample C; □: sample D; ◆: sample E; ◇: sample F.

A: 1000 ml ultra pure water, closed

B: 1000 ml ultra pure water, open to the atmosphere

C: 500 ml, containing FA 2 mg L⁻¹, uranium 1 mg L⁻¹, open to the atmosphere, pH 7

D: 500 ml, containing HA 2 mg L⁻¹, uranium 1 mg L⁻¹, open to the atmosphere, pH 7

E: 500 ml, containing NaNO₃ 0.01 mol L⁻¹, uranium 1 mg L⁻¹, closed, pH 9

F: 500 ml, containing NaNO₃ 0.01 mol L⁻¹, uranium 1 mg L⁻¹, open to the atmosphere, pH 9

According to the results shown in Figure 1, the assessment of the impact of CO₂ on uranium speciation in the model solutions used in the thesis is based on the facts as follows:

1. The background CO₃²⁻ concentration in the model solutions is about 0.5 mg L⁻¹
2. The CO₃²⁻ concentration after 3 hours is less than 1 mg L⁻¹ for U-NaNO₃ model solutions (pH 9), which are open to atmosphere.
3. The CO₃²⁻ concentration after 92 hours is less than 2 mg L⁻¹ for U-NaNO₃ model solutions (pH 9), which are open to atmosphere.
4. The CO₃²⁻ concentration after 24 hours is less than 1 mg L⁻¹ for U-NaNO₃ model solutions (pH 9), which are closed.
5. The CO₃²⁻ concentration after 92 hours is less than 1 mg L⁻¹ for U-HA and U-FA model solutions, which are open to atmosphere.

An assumption for the assessment is that the absorption of atmospheric CO₂ in the model solutions at high pH is faster than that at low pH. The maximum possible concentrations of carbonate in model solutions are presented in Table 2. The concentrations of reagents used in the experiments are presented in Table 3. The distribution of uranium species has been calculated using Visual Minteq program.

Table 2 Maximum possible concentration of carbonate in model solutions.

Experiment	Experimental time	Container	Maximum possible CO ₃ ²⁻ concentration
Determination of diffusion coefficient	~2 hours for U-NaNO ₃ , Several days for U-HA (pH 7)	Open	1 mg L ⁻¹ for U-NaNO ₃ ; equilibrated with atmospheric CO ₂ for U-HA*
Uranium uptake by DGT binding layers	~24 hours	Closed	1 mg L ⁻¹
DGT	< 24 hours for most of samples	Closed	1 mg L ⁻¹
CLEM	~2 hours	Open	1 mg L ⁻¹

*The experimental time is about one week; therefore the U-HA is considered to be at equilibrium with atmospheric CO₂.

Table 3 Concentrations of reagents used in the experiments

Experiment	Model solutions		
	U-NaNO ₃	U-HA	U-FA
Determination of diffusion coefficient	U: 1 mg L ⁻¹ , pH 2-10 NaNO ₃ : 0.01 mol L ⁻¹	U: 2 mg L ⁻¹ , HA: 10 mg L ⁻¹ pH 7	NU*
Uranium uptake by DGT binding layers	U: 0.1 mg L ⁻¹ , pH 2-10 NaNO ₃ : 0.01 mol L ⁻¹	NU	NU
DGT	U: 0.1 mg L ⁻¹ , pH 7 NaNO ₃ : 0.01 mol L ⁻¹ (reference model solution)	U: 0.1 mg L ⁻¹ , HA: 0.1-20 mg L ⁻¹ pH 7	U: 0.1 mg L ⁻¹ , FA: 0.1-10 mg L ⁻¹ pH 7
CLEM	NU	U: 0.02 mg L ⁻¹ , HA: 0.2, 2 and 20 mg L ⁻¹ pH 6, 7 and 8 NH ₄ Ac 0.01 mol L ⁻¹	NU

*NU: not used in the experiment.

Uranium speciation in presence of atmospheric CO₂

Table 4 presents the distribution of uranium species in U-NaNO₃ model solutions. However it cannot be used to interpret the experimental condition because there is carbonate background, which may be from the reagents in all model solutions. Table 5 presents the distribution of uranium species in U-NaNO₃ model solutions containing 0.5 mg L⁻¹ carbonate, which is the background carbonate concentration.

Table 6 presents distribution of uranium species in U-NaNO₃ model solutions containing 1 mg L⁻¹ carbonate. Comparing Table 6 with Table 5, it has been found that for U-NaNO₃ model solutions, when pH is less than 6, the difference between the distribution of uranium species in presence of background carbonate and that in presence of atmospheric CO₂ is less than about 0.5 %; when pH is equal or higher than 6, the difference between the two conditions is less than about 10%. For example, at pH 6, (UO₂)₃(OH)₅⁺ decreases from 47.7% (0.5 mg L⁻¹ CO₃²⁻) to 38.1% (1 mg L⁻¹ CO₃²⁻). Those results can be used to explain the impact of atmospheric CO₂ on the experiments of the determination of diffusion coefficient, the uranium uptake by DGT binding layers and the DGT deployment in reference model solution.

Table 7 presents the distribution of uranium species in model solutions used for determination of uranium diffusion coefficients in U-HA (HA 10 mg L⁻¹) model solutions. The results indicate that the U-HA species is the major species in those model solutions (> 95%), even if the model solutions are equilibrated with atmospheric CO₂.

Tables 8-10 present the uranium speciation in model solutions (HA: 0.2, 2 and 20 mg L⁻¹) used in CLEM experiments, in which ammonium acetate buffer was used. Comparing 0.5 mg L⁻² CO₃²⁻ with 1 mg L⁻¹ CO₃²⁻, it has been found that the distribution of uranium species in presence of atmospheric CO₂ changes less than about 10% in the model solutions containing 0.2 mg L⁻¹ humic acid. When humic acid concentration is 2 mg L⁻¹ or 20 mg L⁻¹, the distribution of uranium species changes very little.

Figures 2-3 show the distribution of uranium species in humic acid model solutions used in DGT experiments. Comparing figure 2 (0.5 mg L⁻¹ CO₃²⁻) with 3 (1 mg L⁻¹ CO₃²⁻), it has been found that there is no significant effect of atmospheric CO₂ on those experiments when humic acid concentration is higher than 0.6 mg L⁻¹. When humic acid concentration is less than 0.6 mg L⁻¹, the distribution of uranium species may be affected by atmospheric CO₂.

Figures 4-5 show the distribution of uranium species in fulvic acid model solutions used in DGT experiments. Comparing figure 4 (0.5 mg L⁻¹ CO₃²⁻) with 5 (1 mg L⁻¹ CO₃²⁻), it has been found that there is no significant effect of atmospheric CO₂ on those experiments when fulvic acid concentration is higher than 1 mg L⁻¹.

The overall assessment of the impact of atmospheric CO₂ on uranium speciation in those model solutions used in the thesis is presented in Table 11.

U-Na₂CO₃ and U-NaHCO₃ model solutions, which were used in determination of uranium diffusion coefficients, have not been discussed because the concentrations of

Na_2CO_3 and NaHCO_3 were very high ($\sim 1000 \text{ mg L}^{-1}$) comparing with the absorption of atmospheric CO_2 during the experiment. For the same reason, the U- NaHCO_3 model solutions used in DGT and CLEM experiments have not been discussed. The impact of atmospheric CO_2 is negligible for those model solutions.

Conclusions

There is significant absorption of the atmospheric CO_2 in sample F because it is at high pH and open to atmosphere. The significant absorption of the atmospheric CO_2 in sample E is probably due to the inleakage of air. The absorption of the atmospheric CO_2 by other samples is less significant, especially for the shorter experimental time. The initial carbonate in model solutions ($\sim 0.5 \text{ mg L}^{-1}$) is probably from reagents. The impact of atmospheric CO_2 needs to be considered for the interpretation of the data presented in the thesis:

- 1) Determination of diffusion coefficient: there is no atmospheric CO_2 effect on the determination of uranium diffusion coefficients in U-HA model solutions and in U- NaNO_3 model solutions if the pH is less than 6. The diffusion coefficients of uranium in the model solutions at $\text{pH} \geq 6$ might be affected by atmospheric CO_2 .
- 2) Uranium uptake by DGT binding layers: there is no atmospheric CO_2 effect on uranium speciation at $\text{pH} < 6$.
- 3) DGT experiments: as discussed earlier, there is some effect of CO_2 on the uranium uptake by DGT in U-HA ($\text{HA} < 0.6 \text{ mg L}^{-1}$) and U-FA ($\text{FA} < 1 \text{ mg L}^{-1}$) model solutions.
- 4) CLEM: the atmospheric CO_2 may affect the CLEM experiments, only when HA concentration is 0.2 mg L^{-1} .

Table 4 Distribution of uranium species in model solutions (uranium 1 mg L⁻¹, NaNO₃ 0.01 mol L⁻¹), at different pH,

calculated using computer program Visual Minteq

pH	Distribution of uranium species (%)								
	UO ₂ ²⁺	UO ₂ OH ⁺	(UO ₂) ₂ (OH) ₂ ²⁺	(UO ₂) ₃ (OH) ₃ ⁺	(UO ₂) ₄ (OH) ₄ ⁺	(UO ₂) ₃ (OH) ₇ ⁻	UO ₂ (OH) ₄ ²⁻	UO ₂ (OH) ₂ (aq)	UO ₂ (OH) ₃ ⁻
2	98.8								
3	98.3	0.4							
4	94.7	3.9	0.1						
5	65.6	27.0	5.0	1.0				0.3	
6	5.5	22.5	3.5	60.6	4.8			2.6	
7	0.1	5.2	0.2	74.2	13.6	0.2		5.9	0.5
8		1.0		49.8	17.2	11.1		11.1	9.8
9		0.1		1.3	0.3	28.8		7.1	62.4
10						1.1	0.9		96.9

Table 5 Distribution of uranium species in model solutions (uranium 1 mg L⁻¹, NaNO₃ 0.01 mol L⁻¹, CO₃²⁻ 0.5 mg L⁻¹), at different pH, calculated using computer program Visual Minteq

pH	Distribution of uranium species (%)							
	UO ₂ ²⁺	UO ₂ OH ⁺	(UO ₂) ₂ (OH) ₂ ²⁺	(UO ₂) ₃ (OH) ₅ ⁺	(UO ₂) ₂ CO ₃ (OH) ₃ ⁻	UO ₂ CO ₃ (aq)	UO ₂ (OH) ₂ (aq)	UO ₂ (OH) ₃ ⁻
2	98.8							
3	98.3	0.4						
4	94.7	3.9						
5	65.2	26.9	5.0	1.0		0.6		
6	5.0	20.8	3.0	47.7	14.0	3.2	2.4	
7		3.2		17.3	72.3	1.1	3.6	
8				2.0	89.7		3.8	3.4
9					65.5		3.2	28.4
10					5.0		1.0	92.1

Table 6 Distribution of uranium species in model solutions (uranium 1 mg L⁻¹, NaNO₃ 0.01 mol L⁻¹, CO₃²⁻ 1 mg L⁻¹), at different pH, calculated using program Visual Minteq

pH	Distribution of uranium species (%)							
	UO ₂ ²⁺	UO ₂ OH ⁺	(UO ₂) ₂ (OH) ₂ ²⁺	(UO ₂) ₃ (OH) ₃ ⁺	(UO ₂) ₂ CO ₃ (OH) ₃ ⁻	UO ₂ CO ₃ (aq)	UO ₂ (OH) ₂ (aq)	UO ₂ (OH) ₃ ⁻
2	98.8							
3	98.3	0.4						
4	94.7	3.9						
5	64.8	26.7	4.9	1.0		1.2		
6	4.7	19.3	2.6	38.1	24.2	6.0	2.2	
7	0.1	2.4		7.0	85.3	1.7	2.7	0.2
8		0.2			93.8		2.6	2.3
9		0.0			75.5		2.4	20.8
10					9.2		1.0	88.1

Table7 Distribution of uranium species in model solutions for determination of uranium diffusion coefficients (uranium 2 mg L⁻¹, humic acid 10 mg L⁻¹), at pH 7, calculated using computer program Visual Minteq

CO ₃ ²⁻ concentration (mg L ⁻¹)	Distribution of uranium species	
	U-HA species	U-carbonate species
0.5	~99%	(UO ₂) ₂ CO ₃ (OH) ₃ ⁻ 0.5%
1 Equilibrated with atmosphere	~98%	(UO ₂) ₂ CO ₃ (OH) ₃ ⁻ 0.9%
		UO ₂ CO ₃ (aq) 0.1%
	~95%	(UO ₂) ₂ CO ₃ (OH) ₃ ⁻ 3.4%
		UO ₂ CO ₃ (aq) 0.6%

Table 8 Distribution of uranium species in model solutions for CLEM (uranium 20 $\mu\text{g L}^{-1}$, humic acid 0.2 mg L^{-1} , NH_4Ac 0.01 mol L^{-1}) at pH 6,7 and 8, calculated using computer program Visual Minteq

CO_3^{2-} concentration (mg L^{-1})	pH	Distribution of uranium species (%)			
		U-HA species	U-Acetate species	U-carbonate species	Other U species
0.5	6	52.7	35.4	10.5	1.3
	7	43.0	5.5	25.9	25.6
	8	16.0	0.1	49.1	34.8
1	6	52.3	34.7	2.6	10.3
	7	39.8	4.5	35.3	10.3
	8	14.7	0.1	58.6	26.7

Table 9 Distribution of uranium species in model solutions for CLEM (uranium 20 $\mu\text{g L}^{-1}$, humic acid 2 mg L^{-1} , NH_4Ac 0.01 mol L^{-1}) at pH 6,7 and 8, calculated using computer program Visual Minteq

CO_3^{2-} concentration (mg L^{-1})	pH	Distribution of uranium species (%)			
		U-HA species	U-Acetate species	U-carbonate species	Other U species
0.5	6	98.7	1.0	0.0	0.3
	7	99.1	0.1	0.1	0.6
	8	91.2	~0	2.0	6.7
1	6	98.7	1.0	0.1	0.3
	7	98.9	0.1	0.3	0.6
	8	89.8	~0	3.7	6.4

Table 10 Distribution of uranium species in model solutions for CLEM (uranium 20 $\mu\text{g L}^{-1}$, humic acid 20 mg L^{-1} , NH_4Ac 0.01 mol L^{-1}) at pH 6,7 and 8, calculated using computer program Visual Minteq

CO_3^{2-} concentration (mg L^{-1})	pH	Distribution of uranium species (%)		
		U-HA species	U-Acetate species	U-carbonate species
0.5	6	~100%		
	7	~100%		
	8	~100%		
1	6	~100%		
	7	~100%		
	8	~100%

Figure 2 Distribution of uranium species in humic acid model solution with carbonate.
pH 7
U: 0.1 mg L⁻¹,
Humic acid: 0-1 mg L⁻¹
CO₃²⁻: 0.5 mg L⁻¹
◆: U-humic acid species; ▲: U-carbonate species; ●: Other uranium species

Figure 3 Distribution of uranium species in humic acid model solution with carbonate.
pH 7
U: 0.1 mg L⁻¹,
Humic acid: 0-1 mg L⁻¹
CO₃²⁻ : 1 mg L⁻¹
◆: U-humic acid species; ▲: U-carbonate species; ●: Other uranium species

Figure 4 Distribution of uranium species in fulvic acid model solution with carbonate.

pH 7

U: 0.1 mg L⁻¹,

Fulvic acid: 0-2 mg L⁻¹

CO₃²⁻: 0.5 mg L⁻¹

◆: U-fulvic acid species; ▲: U-carbonate species; ●: Other uranium species

Figure 5 Distribution of uranium species in fulvic acid model solution with carbonate.
pH 7
U: 0.1 mg L⁻¹,
Fulvic acid: 0-2 mg L⁻¹
CO₃²⁻: 1 mg L⁻¹
◆: U-fulvic acid species; ▲: U-carbonate species; ●: Other uranium species

Table 11 Overall assessment of the impact of atmospheric CO₂ on the model solutions used in the thesis.

Experiment	Uranium model solutions		
	U-NaNO ₃	U-HA	U-FA
Determination of diffusion coefficients	when pH ≥ 6	not significant (HA is 10 mg L ⁻¹)	NU*
Uranium uptake by DGT binding layers	when pH ≥ 6	NU	NU
DGT	In reference model solution	when HA < 0.6 mg L ⁻¹	when FA < 1 mg L ⁻¹
CLEM	NU	when HA is 0.2 mg L ⁻¹	NU

*NU: not used in the experiment

Appendix B - Stability constants of uranium species

Stability Constants of uranium species used in Visual Minteq program

Uranium species	Reaction	log K	Reference
$\text{UO}_2\text{Ac}_2(\text{aq})^*$	$\text{UO}_2^{2+} + 2\text{Ac}^- \leftrightarrow \text{UO}_2\text{Ac}_2$	5.04	NIST[1]
UO_2Ac_3^-	$\text{UO}_2^{2+} + 3\text{Ac}^- \leftrightarrow \text{UO}_2\text{Ac}_3^-$	7.06	NIST
$\text{UO}_2(\text{CO}_3)_2^{2-}$	$\text{UO}_2^{2+} + 2\text{CO}_3^{2-} \leftrightarrow \text{UO}_2(\text{CO}_3)_2^{2-}$	16.61	NEA_2003 [2]
$\text{UO}_2(\text{CO}_3)_3^{4-}$	$\text{UO}_2^{2+} + 3\text{CO}_3^{2-} \leftrightarrow \text{UO}_2(\text{CO}_3)_3^{4-}$	21.84	NEA_2003
$\text{UO}_2(\text{OH})_2(\text{aq})$	$\text{UO}_2^{2+} + 2\text{H}_2\text{O} \leftrightarrow \text{UO}_2\text{OH}_2 + 2\text{H}^+$	-12.15	NEA_2003
$\text{UO}_2(\text{OH})_3^-$	$\text{UO}_2^{2+} + 3\text{H}_2\text{O} \leftrightarrow \text{UO}_2(\text{OH})_3^- + 3\text{H}^+$	-20.25	NEA_2003
$\text{UO}_2(\text{OH})_4^{2-}$	$\text{UO}_2^{2+} + 3\text{H}_2\text{O} \leftrightarrow \text{UO}_2(\text{OH})_4^{2-} + 4\text{H}^+$	-32.4	NEA_2003
$\text{UO}_2\text{CO}_3(\text{aq})$	$\text{UO}_2^{2+} + \text{CO}_3^{2-} \leftrightarrow \text{UO}_2\text{CO}_3$	9.94	NEA_2003
UO_2OH^+	$\text{UO}_2^{2+} + \text{H}_2\text{O} \leftrightarrow \text{UO}_2\text{OH}^+ + \text{H}^+$	-5.25	NEA_2003
$(\text{UO}_2)_2(\text{OH})_2^{2+}$	$2\text{UO}_2^{2+} + 2\text{H}_2\text{O} \leftrightarrow (\text{UO}_2)_2(\text{OH})_2^{2+} + 2\text{H}^+$	-5.62	NEA_2003
$(\text{UO}_2)_2\text{OH}_3^+$	$2\text{UO}_2^{2+} + 3\text{H}_2\text{O} \leftrightarrow (\text{UO}_2)_2(\text{OH})_3^+ + 3\text{H}^+$	-2.7	NEA_2003
$(\text{UO}_2)_3(\text{CO}_3)_6^{6-}$	$3\text{UO}_2^{2+} + 6\text{CO}_3^{2-} \leftrightarrow (\text{UO}_2)_3(\text{CO}_3)_6^{6-}$	54	NEA_2003
$(\text{UO}_2)_3(\text{OH})_4^{2+}$	$3\text{UO}_2^{2+} + 4\text{H}_2\text{O} \leftrightarrow (\text{UO}_2)_3(\text{OH})_4^{2+} + 4\text{H}^+$	-11.9	NEA_2003
$(\text{UO}_2)_3(\text{OH})_5^+$	$3\text{UO}_2^{2+} + 5\text{H}_2\text{O} \leftrightarrow (\text{UO}_2)_3(\text{OH})_5^+ + 5\text{H}^+$	-15.55	NEA_2003
$(\text{UO}_2)_3(\text{OH})_7^-$	$3\text{UO}_2^{2+} + 7\text{H}_2\text{O} \leftrightarrow (\text{UO}_2)_3(\text{OH})_7^- + 7\text{H}^+$	-32.2	NEA_2003
$(\text{UO}_2)_4(\text{OH})_7^+$	$4\text{UO}_2^{2+} + 7\text{H}_2\text{O} \leftrightarrow (\text{UO}_2)_4(\text{OH})_7^+ + 7\text{H}^+$	-21.9	NEA_2003
$\text{Ca}_2\text{UO}_2(\text{CO}_3)_3(\text{aq})$	$2\text{Ca}^{2+} + \text{UO}_2^{2+} + 3\text{CO}_3^{2-} \leftrightarrow \text{Ca}_2\text{UO}_2(\text{CO}_3)_3$	30.7	[3]
$\text{CaUO}_2(\text{CO}_3)_3^{2-}$	$\text{Ca}^{2+} + \text{UO}_2^{2+} + 3\text{CO}_3^{2-} \leftrightarrow \text{Ca}_2\text{UO}_2(\text{CO}_3)_3^{2-}$	27.18	[3]

* The abbreviation Ac refers to acetyl group

References:

1. Critical Stability Constants of Metal Complexes Database (CRITICAL) published by the National Institute of Standards and Technology
2. Guillaumont, R., and Editor (2003). Update on the Chemical Thermodynamics of Uranium, Neptunium, Plutonium, Americium and Technetium.
3. Dong, W., and Brooks Scott, C. (2006). Determination of the formation constants of ternary complexes of uranyl and carbonate with alkaline earth metals (Mg^{2+} , Ca^{2+} , Sr^{2+} , and Ba^{2+}) using anion exchange method. Environmental science & technology 40, 4689-4695.