

1-1-2002

Evaluation of the diffusion gradient in thin-films (DGT) technique for measuring trace metal concentrations in freshwaters

Deborah Lynn Parent
Ryerson University

Follow this and additional works at: <http://digitalcommons.ryerson.ca/dissertations>

 Part of the [Environmental Engineering Commons](#)

Recommended Citation

Parent, Deborah Lynn, "Evaluation of the diffusion gradient in thin-films (DGT) technique for measuring trace metal concentrations in freshwaters" (2002). *Theses and dissertations*. Paper 3.

This Thesis is brought to you for free and open access by Digital Commons @ Ryerson. It has been accepted for inclusion in Theses and dissertations by an authorized administrator of Digital Commons @ Ryerson. For more information, please contact bcameron@ryerson.ca.

EVALUATION OF THE DIFFUSION GRADIENT IN THIN-FILMS (DGT) TECHNIQUE
FOR MEASURING TRACE METAL CONCENTRATIONS IN FRESHWATERS

by

Deborah Lynn Parent

A thesis

presented to Ryerson University

in partial fulfillment of the
requirement for the degree of
Master of Applied Science

in the program of
Environmental Applied Science and Management

Toronto, Ontario, Canada, 2002

©Deborah Lynn Parent, 2002



National Library
of Canada

Bibliothèque nationale
du Canada

Acquisitions and
Bibliographic Services

Acquisitions et
services bibliographiques

395 Wellington Street
Ottawa ON K1A 0N4
Canada

395, rue Wellington
Ottawa ON K1A 0N4
Canada

Your file Votre référence

ISBN: 0-612-85324-1

Our file Notre référence

ISBN: 0-612-85324-1

The author has granted a non-exclusive licence allowing the National Library of Canada to reproduce, loan, distribute or sell copies of this thesis in microform, paper or electronic formats.

L'auteur a accordé une licence non exclusive permettant à la Bibliothèque nationale du Canada de reproduire, prêter, distribuer ou vendre des copies de cette thèse sous la forme de microfiche/film, de reproduction sur papier ou sur format électronique.

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

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

Canada

I hereby declare that I am the sole author of this thesis.

I authorize Ryerson Polytechnic University to lend this thesis to other institutions or individuals for the purpose of scholarly research.

I further authorize Ryerson Polytechnic University to reproduce this thesis by photocopying or by other means, in total or in part, at the request of other institutions or individuals for the purpose of scholarly research.

Ryerson Polytechnic University requires the signatures of all persons using or photocopying this thesis. Please sign below, and give address and date.

ABSTRACT

EVALUATION OF THE DIFFUSION GRADIENT IN THIN-FILMS (DGT) TECHNIQUE

FOR MEASURING TRACE METAL CONCENTRATIONS IN FRESHWATERS

The recently developed Diffusion Gradient in Thin-films (DGT) technique is based on a simple device that accumulates metals *in situ*, over time in a Na resin gel. Metal ions diffuse through a hydrogel membrane and are rapidly bound by the resin. The many advantages associated with the DGT technique (simplicity, *in situ* technique, low detection limits, and ability to measure many metals) have lead to its rapid application in aquatic environments.

Caveats have been recognized with the DGT technique when it is used in aquatic environments. These include: the ability of strongly complexed organic-metal molecules to diffuse through the hydrogel and become complexed by the resin gel, and in freshwater lakes with a low concentration of cations ($\Sigma [\text{cations}] \leq 2 \times 10^{-4} \text{ M}$), it is hypothesized that the diffusion coefficient of metal ions entering the DGT device increases. Both of these caveats overestimate the concentrations of labile inorganic metals in the deployment solution.

The hypothesis that deploying DGT devices equipped with two different hydrogel formulations (“open” and “tight”) will provide reasonable measurements of DGT-labile “organic” and “inorganic” concentrations of Mn, Cd and Pb was tested in the field. DGT devices were deployed in three lakes (Lake Tantaré, Lake St. Joseph and Lake Memphremagog). To compare the responses of the DGT devices with the total dissolved metal concentration ($< 0.20 \mu\text{m}$) of each lake, *in situ* dialysis samplers were deployed simultaneously. Overestimation of DGT-labile “inorganic” concentrations of Mn and Pb, and overestimation of DGT-labile “organic” Cd was observed when compared to the measured total dissolved metal concentrations in the lakes.

The hypothesis that DGT devices equipped with a Ca form of the resin gel (as an alternative to the sodium based resin gel in the DGT device) will reasonably measure Mn, Cd and Pb labile metal concentrations in freshwater lakes with low cation concentrations was tested. DGT devices with the Ca form of the resin gel were deployed in Lake Tantaré, Lake St. Joseph and Lake Memphremagog. Overestimation of DGT-labile metal concentrations of Mn, Cd and Pb were observed with the Ca resin gel in the lakes when compared to the measured total dissolved concentrations.

The implication of these findings is that the DGT technique should not be used in freshwaters with low cation concentrations ($\Sigma [\text{cations}] \leq 2 \times 10^{-4} \text{ M}$), typical of lakes found in the Canadian environment, until the caveats of the technique have been resolved. Extreme caution should be used when drawing conclusions regarding the concentrations of inorganic and organic metal species, since it has been found the DGT devices with the two different hydrogel formulations overestimate the inorganic metal concentration relative to the organic metal concentration in aquatic environments.

ACKNOWLEDGEMENTS

I would like to acknowledge Michael Twiss for his supervision and for providing me with the opportunity to conduct my Masters thesis in aquatic sciences. Not only did he provide me with the opportunity to further develop my scientific research skills in both field and laboratory studies, he encouraged professional development in the form of financial support at various conferences. I would also like to thank him for encouraging excellence in all avenues of my research, and for giving me with the confidence to work independently and to trust my own judgment.

I am indebted to Richard Goulet for all of his assistance. His efforts in facilitating the field study, preparing the *in situ* dialysis samplers, answering my many questions and providing me with timely advice, were all greatly valued.

I would also like to thank André Tessier and his research assistants at the INRS-ETE. They provided me with a location and the necessary equipment required to conduct the field study, gave up their time to filter and analyze water samples, and were extremely helpful throughout the field study.

Funding for this research was provided by grants from the Toxic Substance Research Initiative (TSRI) and from the Natural Sciences and Engineering Research Council of Canada (NSERC) awarded to Michael Twiss and André Tessier.

I would like to thank the graduate students for making my time at Ryerson fun and enjoyable. In particular, special thanks to Tara Patey for analyzing many of my samples, and Jennifer Stewart for providing me with advice and assistance.

Finally, I would like to thank my parents who supported and encouraged me, my friends for listening, and Jim for his enduring patience and understanding.

TABLE OF CONTENTS

CHAPTER 1: INTRODUCTION.....	1
1.1 TRACE METALS IN FRESHWATER ENVIRONMENTS.....	1
1.2 THE FREE-ION ACTIVITY MODEL (FIAM)	2
1.3 TECHNIQUES COMMONLY USED TO MEASURE METAL SPECIATION IN AQUATIC ENVIRONMENTS.....	3
1.3.1 Thermodynamic Modelling.....	3
1.3.2 Electrochemical Methods.....	4
1.3.3 Non Electrochemical Methods	5
1.4. DGT THEORY	7
1.4.1 Lability Distinction.....	10
1.4.2 Measurement of DGT-labile Species.....	10
1.4.3 Measurement of DGT-Labile “Inorganic” Species.....	13
1.5. LABORATORY STUDIES.....	13
1.5.1 Development of the DGT Technique	13
1.5.2 Effect of Solution Conditions on the Diffusion Coefficients in the Hydrogel	15
1.5.3 Measurement of DGT-labile Organic Complexes by the DGT Device.....	16
1.5.4 Estimates of DGT-labile “Organic” and “Inorganic” Species	17
1.5.5 Behaviour of Metals in the DGT Devices	18
1.6 FIELD APPLICATIONS OF THE DGT TECHNIQUE TO AQUATIC ENVIRONMENTS	20
1.7 REVIEW OF CURRENT STATE OF DGT KNOWLEDGE	24
1.8 THESIS OBJECTIVES	24
1.9 SCOPE OF STUDY	25
1.10 HYPOTHESES.....	26
1.11 OUTLINE OF THESIS	27
CHAPTER 2: STANDARD METHODS	29
2.1 WATER SYSTEM.....	29
2.2 TRACE-METAL CLEAN TECHNIQUE	29
2.3 WASHING PROCEDURES	30
2.3.1 Metals.....	30
2.3.2 Organics	30
2.4 PREPARATION OF TRACE-METAL CLEAN SOLUTIONS.....	30
2.5 FORMULATION OF HYDROGELS.....	31
2.5.1 Stock Solution Preparation.....	32
2.5.2 Hydrogel Preparation	32
2.6 GRAPHITE FURNACE ATOMIC ABSORPTION SPECTROSCOPY TECHNIQUE.....	33
CHAPTER 3: BEHAVIOUR OF MN, CD, PB AND ORGANIC MATTER IN HYDROGELS	34
3.1 INTRODUCTION.....	34
3.2 METHODS.....	37
3.2.1 Formulation of Hydrogels	37
3.2.2 Trace Metal Experiments	37
3.2.3 Organic Experiments.....	40
3.3. RESULTS.....	43
3.3.1 Trace Metal Experiments	43
3.3.2 Organic Experiments.....	45
3.4. DISCUSSION.....	47
3.4.1 Behaviour of Metals in Hydrogels.....	47
3.4.2 Behaviour of Organic Matter in Hydrogels.....	49
3.4.3 Conclusion.....	52

CHAPTER 4: THE EFFECT OF RESIN GEL FORMULATION AND BULK SOLUTION CATION CONCENTRATION ON THE EFFECTIVE DIFFUSION COEFFICIENTS OF MN, CD AND PB	53
4.1 INTRODUCTION	53
4.2 METHODS.....	54
4.2.1 Preparation of Resin Gels and Hydrogels.....	54
4.2.2 Experiments.....	56
4.3. RESULTS.....	60
4.3.1 Determination of Residual Na in the Ca-based Resin Gels.....	60
4.3.2 Determination of the Diffusive Layer	61
4.3.3 Elution Efficiency.....	62
4.3.4 Effect of Bulk Solution Cation Concentration on the Diffusion Coefficients of Mn, Cd and Pb	62
4.3.5 Comparison of Na-based and Ca-based Resin Gels.....	64
4.3.6 Effect of the Compositions of the Bulk Solutions on the Performance of Na-based and Ca-based DGT Devices	65
4.4 DISCUSSION.....	65
4.4.1 Effect of Cation Concentration on the diffusion coefficients of Mn, Cd, and Pb.....	65
4.4.2 Comparison of Na-based and Ca-based DGT Devices	67
4.4.3 Effect of the Composition of Bulk Solution on the Diffusion Coefficients of Mn, Cd and Pb.....	68
4.4.4 Reconciliation with Previous Studies	69
4.4.5 Recommendations for Future Research	71
4.4.6 Conclusions	71
CHAPTER 5: IN SITU DGT EXPERIMENTS	72
5.1 INTRODUCTION	72
5.2 METHODS.....	74
5.2.1 DGT Devices	74
5.2.2 In Situ Dialysis	76
5.2.3 Field Deployments of DGT devices and In Situ Dialysis Samplers.....	76
5.2.4 Calculation of DGT-labile “Organic” and “Inorganic” Concentrations.....	78
5.2.5 Water Quality Parameters.....	79
5.3. RESULTS.....	79
5.3.1 Water Quality Parameters.....	79
5.3.2 Determination of Diffusive Boundary Layer (dbl) and Diffusive Layer	80
5.3.3 In Situ Measurements of Labile “Organic” and “Inorganic” Metals in Lakes Tantaré, St. Joseph, and Memphremagog.....	81
5.3.4 In Situ Measurements of DGT-labile “Inorganic” Metal Species in Lakes Tantaré, St. Joseph, and Memphremagog.....	88
5.3.5 Comparison of Na-based and Ca-based DGT devices	89
5.4 DISCUSSION.....	91
5.4.1 In Situ Measurements of Labile “Inorganic” and “Organic” Metals in Lakes Tantaré, St. Joseph, and Memphremagog.....	91
5.4.2 In Situ Measurements of DGT-labile “Inorganic” Metal Species in Lakes Tantaré, St. Joseph, and Memphremagog.....	96
5.4.3 Determination of DGT-labile “Inorganic” Mn, Cd and Pb Using Ca-based DGT Devices.....	100
5.4.4 Effect of the Diffusion Coefficients of Metals in the Diffusive Boundary Layer on DGT-labile Metal Calculations	104
5.4.5 Conclusions	105
CHAPTER 6: EVALUATION OF THE DGT TECHNIQUE	107
6.1 CAVEATS ASSOCIATED WITH THE DGT TECHNIQUE	107
6.2 REVIEW OF EXPERIMENTAL METHODS AND TECHNIQUES.....	107
6.3 SUMMARY OF FINDINGS	108
6.4 CONCLUSIONS.....	109
6.5 EVALUATION OF TECHNIQUE.....	110
APPENDIX.....	112
REFERENCES.....	113

LIST OF TABLES

Table 1. <i>Preparation of clean Na Chelex-100</i>	31
Table 2. <i>Concentration of major cations and pH in Lakes Tantaré, St. Joseph and Memphremagog.</i>	38
Table 3. <i>Mean apparent tracer diffusion coefficients of Mn, Cd and Pb in "open" and "tight" hydrogels for Lakes Tantaré, St. Joseph, and Memphremagog.</i>	44
Table 4. <i>Mean K_d values for Mn, Cd, and Pb in "open" and "tight" hydrogels for Lakes "Tantaré, St. Joseph, and Memphremagog.</i>	45
Table 5. <i>Mean water content of hydrogels.</i>	45
Table 6. <i>Mean apparent tracer diffusion coefficients of organics in "open" and "tight" hydrogels for Lakes Tantaré, St. Joseph, and Memphremagog.</i>	46
Table 7. <i>Mean fulvic acid K_d values for "open" and "tight" hydrogels in Lakes Tantaré, St. Joseph, Memphremagog.</i>	47
Table 8. <i>Experimental variables for the deployment of Na-based and Ca-based DGT devices in 20 L solutions.</i>	59
Table 9. <i>Residual Na concentration in a Ca-based resin gel after 5 exchanges with CaCl_2 solution over a 5 day period.</i>	60
Table 10. <i>Mean elution factors for the efficiency of 5 mL of 2 M HNO_3 for eluting Mn, Cd, and Pb from Na-based resin gels and Ca-based resin gels.</i>	62
Table 11. <i>Mean diffusion coefficients of Mn, Cd, and Pb in DGT devices with 0.10-cm "tight" hydrogels deployed in solutions of different cation concentration.</i>	63
Table 12. <i>Mean diffusion coefficients of Mn, Cd and Pb in 2×10^{-5} M $\text{Ca}(\text{NO}_3)_2$ using DGT devices with 0.10-cm "open" hydrogels.</i>	65
Table 13. <i>Water quality parameters measured in Lakes Tantaré, St. Joseph, and Memphremagog.</i>	80
Table 14. <i>Determination of the mean diffusive boundary layer and diffusive layer (cm) for Lakes Tantaré, St. Joseph, and Memphremagog.</i>	81
Table 15. <i>Mean DGT-labile "organic" and "inorganic" concentrations of Mn, Cd, and Pb in Lakes Tantaré, St. Joseph, and Memphremagog.</i>	87
Table 16. <i>Mean concentration of DGT-labile "inorganic" Mn, Cd and Pb in Lakes Tantaré, St. Joseph, and Memphremagog using Na-based DGT devices and Ca-based DGT devices.</i>	89

LIST OF FIGURES

Figure 1. <i>Concentration gradient in a DGT device.</i>	8
Figure 2. <i>Schematic diagram of the diaphragm diffusion cell.</i>	36
Figure 3. <i>Schematic diagram of DGT device.</i>	59
Figure 4. <i>Graphical determination of the diffusive boundary layer for a 20L carboy....</i>	61
Figure 5. <i>Diagram of DGT assembly.</i>	75
Figure 6. <i>Graphical determination of the diffusive boundary layers for Lakes Tantaré, St. Joseph and Memphremagog.</i>	80
Figure 7. <i>Determination of DGT-labile “organic” and “inorganically” bound Mn in Lake Tantaré.</i>	82
Figure 8. <i>Determination of DGT-labile “organic” and “inorganically” bound Mn in Lake St. Joseph.</i>	83
Figure 9. <i>Determination of DGT-labile “organic” and “inorganically bound Mn in Lake Memphremagog.</i>	83
Figure 10. <i>Determination of DGT-labile “organic” and “inorganically” bound Cd in Lake Tantaré.</i>	85
Figure 11. <i>Determination of DGT-labile “organic” and “inorganically” bound Cd in Lake St. Joseph.</i>	85
Figure 12. <i>Determination of DGT-labile “organic” and “inorganically bound Cd in Lake Memphremagog.</i>	86
Figure 13. <i>Determination of DGT-labile “organic” and “inorganically” bound Pb in Lake Tantaré.</i>	87

LIST OF EQUATIONS

Equation	Formula	Page
(1)	$[C_b] = M_{DGT} \Delta g / {}^{\text{B}}D \text{At}$	8
(2)	$M_{DGT} = C_e(V_g + V_e)/f_e$	9
(3)	$1/M = \Delta g / D \text{At} [C_b]$	9
(4)	$1/M = \Delta g / D \text{At} [C_b] + \delta / D \text{At} [C_b]$	9
(5)	$t = (\Delta g)^2 / 2 {}^{\text{B}}D$	10
(6)	$M_{DGT} = M_{\text{inorg}} + M_{\text{org}}$	12
(7)	$M_{\text{inorg}} = ({}^{\text{B}}D_{\text{inorg}} C_{\text{inorg}} \text{At}) / \Delta g$	12
(8)	$M_{\text{org}} = ({}^{\text{B}}D_{\text{org}} C_{\text{org}} \text{At}) / \Delta g$	12
(9)	$M_{DGT} = ({}^{\text{B}}D_{\text{inorg}} C_{\text{inorg}} + {}^{\text{B}}D_{\text{org}} C_{\text{org}}) \text{At} / \Delta g$	12
(10)	$M_{DGT} / [(\text{At} / \Delta g) {}^{\text{B}}D_{\text{inorg}}] = C_{\text{inorg}} + ({}^{\text{B}}D_{\text{org}} / {}^{\text{B}}D_{\text{inorg}}) C_{\text{org}}$	12
(11)	$D_{i,\text{eff}} = D_i - D_i z_i C_i \left[\frac{\sum_{j=1}^n z_j D_j \left(\frac{dC_j/dx}{dC_i/dx} \right)}{\sum_{j=1}^n z_j^2 D_j C_j} \right]$	16
(12)	$K_d = {}^{\text{B}}[M] / {}^{\text{W}}[M]$	19
(13)	$C_b = (M_{DGT} / \text{At}) (\Delta g / {}^{\text{B}}D + \gamma / {}^{\text{F}}D + \delta / {}^{\text{W}}D)$	20
(14)	$M = {}^{\text{B}}D (dC / \Delta g) \text{At}$	36
(15)	$dC / \Delta g = ([C]_{\text{source}} - [C]_{\text{sink}}) / \Delta g$	36
(16)	$M = {}^{\text{B}}D \{ ([C]_{\text{source}} - [C]_{\text{sink}}) / \Delta g \} \text{At}$	36
(17)	$\log D_T = \frac{1.37023(T - 25) + 8.36 \times 10^{-4}(T - 25)^2}{109 + T} + \log \frac{D_{25}(273 + T)}{298}$	37
(18)	$K_d = {}^{\text{B}}[\text{Org}] / {}^{\text{W}}[\text{Org}]$	41
(19)	${}^{\text{B}}[\text{Org}] = \Delta {}^{\text{W}}\text{Org} / {}^{\text{W}}V_g$	41
(20)	$\Delta {}^{\text{W}}\text{Org} = {}^{\text{W}}\text{Org}_i - {}^{\text{W}}\text{Org}_f$	42
(21)	$\Phi = {}^{\text{B}}D_{\text{HTO}} / {}^{\text{W}}D_{\text{HTO}}$	43
(22)	$f_e = C_e / C_s$	57
(23)	${}^{\text{B}}D = M_{DGT} \Delta g / [C_b] \text{At}$	60
(24)	$J_{\text{Na}^+} = 2J_{\text{Ca}^{2+}} + 2J_{\text{Mg}^{2+}} + J_{\text{H}^+} + J_{\text{K}^+} + 2J_{\text{divalent trace metals}}$	69

CHAPTER 1: INTRODUCTION

1.1 TRACE METALS IN FRESHWATER ENVIRONMENTS

The major pathways of metals for entrance into freshwater environments are riverine inputs, sewage discharge, specific point sources (industrial effluents) and atmospheric deposition. The relative importance of each of these sources is dependent on the watershed (presence of rivers, and presence/proximity to industrial/commercial activity), and the watershed to surface area ratio (accessible to atmospheric deposition) (Sigg, 1994). In Canada, atmospheric depositions from emissions are a significant source of trace metals to freshwaters in industrial (Nriagu *et al.*, 1998) and remote areas (e.g. Dillon *et al.*, 1982).

Once in the freshwater environment, the fate of trace metals is influenced by their chemical speciation. The speciation of trace metals can be defined as the distribution of the chemical elements between their various chemical species or groups of species (Campbell, 1995). In freshwaters, several chemical species of trace metals can exist. They can exist as:

1. the hydrated “free” ion (H_2O as a ligand);
2. complexes with simple inorganic (e.g. NO_3^- , Cl^- , OH^-) or organic ligands (amino-acids, hydroxy-acids, sugars);
3. complexes with sites of organic macromolecules (humic substances and polysaccharides) or colloids,

or

4. exposed at the surface of suspended particles.

(Buffle and Altman, 1987 and Buffle, 1988).

The speciation of various trace metals has been determined in aquatic environments. Highly reactive metals, such as Cu and Zn, tend to occur fully complexed by organic ligands

(e.g. Wells *et al.*, 1998). Significant levels of organic complexation have also been reported for Pb (Capodaglio *et al.*, 1990) and Hg (Gill and Bruland, 1990) in aquatic environments. Up to 80% of the total dissolved cadmium has been found to exist as the free-metal ion in acidic waters (Xue and Sigg, 1998), although significant complexation by organic matter has also been reported (Wells *et al.*, 1998, Xue and Sigg, 1998).

1.2 THE FREE-ION ACTIVITY MODEL (FIAM)

The biological availability of dissolved trace metals to aquatic organisms can be correlated directly with chemical speciation (Campbell, 1995). In the past 30 years, several laboratory experiments have been conducted to study how uptake, toxicity, and nutrition of trace metals are related to their speciation in the external media. Anderson *et al.* (1978) examined the effects of Zn^{2+} ion on the growth rate of the diatom *Thalassiosira weissflogii*. They found that the growth rate of *T. weissflogii* was affected by, and dependent on, the free- Zn^{2+} ion activity in the medium. In a similar study, Bates *et al.* (1982) studied the adsorption and transport of Zn onto algal surfaces and across the cell membrane of two algal species *Chlamydomonas variabilis* and *Scenedesmus subspicatus*. They confirmed that the activity of the free- Zn^{2+} ion in the media determined its bioavailability to *C. variabilis* and *S. subspicatus*. The results of these and numerous other studies led to the formulation (Morel, 1983) of the free-ion activity model (FIAM) for metal-organism interactions. The FIAM suggests that the physiological effects of metals (uptake, nutrition and toxicity) on an organism are proportional to the metal's free-ion activity rather than the total metal concentration or the complexed metal concentration (Campbell, 1995).

In a study of 28 lakes, Hare and Tessier (1998) found that the free-ion activity model accurately predicted Cd concentrations in the aquatic insect *Chaoborus* in nature. However,

concentrations of Pb in *Chaoborus* could not be linked to the concentration of the free-metal ion. This was attributed to the inability to measure low Pb concentrations in many of the water samples by graphite furnace atomic absorption spectrophotometry (Hare and Tessier, 1998).

Since physiological effects of many metals to organisms have been linked to the free-metal ion activity and since the concentrations of many trace metals in aquatic environments are below the analytical limits of detection, a strong interest has developed in the advancement and use of thermodynamic models and analytical methods to determine and predict the chemical speciation and concentration of low level trace metals in aquatic environments.

1.3 TECHNIQUES COMMONLY USED TO MEASURE METAL SPECIATION IN AQUATIC ENVIRONMENTS

The characterisation of trace metal speciation in aquatic environments can be determined using two different approaches: thermodynamic modeling or direct sample analysis. Thermodynamic modelling provides an indirect method to calculate the speciation of trace metals from measured total dissolved ligand and cation concentrations (Turner, 1995). Direct sample analysis uses electrochemical and non-electrochemical methods to calculate metal speciation in water samples collected in the field and brought back to the laboratory.

1.3.1 Thermodynamic Modelling

Thermodynamic modelling is based on the assumption that the system being modelled is at equilibrium. The validity of the model is dependent on the processes included in the model. Non-equilibrium conditions can be identified in certain cases by comparison with experimental measurements. The accuracy of the calculation is dependent upon the user's ability to identify and quantify all of the ligands present in the natural water sample and on the quality of the thermodynamic database (Turner, 1995). The Windermere Humic Aqueous Model (WHAM), an example of thermodynamic modeling, is a computer program designed to

calculate equilibrium chemical speciation in surface and ground waters, sediments and soils. The model is suitable for use when metal speciation is dominated by complexation with organic ligands (such as humic substances) (Tipping, 1994).

1.3.2. Electrochemical Methods

Electrochemical methods include voltammetry and potentiometry. Voltammetric methods such as anodic stripping voltammetry and adsorptive cathodic stripping voltammetry provide the most direct methods for the study of metal species at low concentration levels (10^{-8} to 10^{-11} M) because they do not require preconcentration at the initial step (Mota and Correia dos Santos, 1995). A greater amount of information can be obtained from voltammetric methods than from potentiometric methods, but the information is more difficult to interpret because of its complexity (Mota and Correia dos Santos, 1995). Potentiometry with an ion selective electrode (ISE) could be one of the most powerful tools in speciation studies because the free-ion activity is usually measured. However, due to the lack of sensitivity of ISE (high detection limit, greater than 10^{-6} M), use of this technique is limited to water polluted with trace metals. Therefore, potentiometric procedures are limited to the major elements (Na, K, Ca, and Cl) whose concentration in aquatic environments lies within the detection range of the ISE (Mota and Correia dos Santos, 1995).

In a comparison study of the ability of Differential Pulse Cathodic Stripping Voltammetry (DP-CSV) and potentiometry with ISE to determine Cu^{2+} concentrations in lake water, Xue and Sunda (1997) found that at low concentrations, the ISE electrode gave erroneously high $[\text{Cu}^{2+}]$ readings due to failure of the electrode membrane to equilibrate with the sample. DP-CSV was useful for measurement at ambient concentrations but it is a much more laborious technique. To determine $[\text{Cu}^{2+}]$ with DP-CSV one must know the ratio of free-

Cu^{2+} ions to both labile inorganic and organic compounds (Xue and Sunda, 1997). The ratio of free- Cu^{2+} ions to labile inorganic compounds can be calculated by knowing simple variables such as $[\text{Cl}^-]$, $[\text{CO}_3^{2-}]$ and pH.

1.3.3 Non Electrochemical Methods

Some of the non-electrochemical methods used to determine metal speciation include: ion-exchange and chelating resins, direct spectroscopic measurement, and size-based separations.

Ion-exchange and chelating resins contain complexing adsorbants, which are used to separate labile metal species from aqueous solutions. The solution of interest is passed through a column packed with the adsorbant. Ion-exchange resins have had limited applications to speciation studies because the separations are based on ionic charge alone, and have failed to demonstrate a relationship to bioavailability (Apte and Batley, 1995). Chelex-100 resin has the greatest application in speciation studies, but the resin may possibly cause destructive effects to the bulk solution. The resin can perturb the metal-complex equilibria of the bulk solution, causing a rapid dissociation of weak complexes and slow dissociation of strong complexes (depending on contact time). Using Chelex-100 separations will therefore overestimate the metal effects on organisms (Apte and Batley, 1995).

Filtration techniques, such as *in situ* dialysis samplers (peepers) and ultrafiltration, separate high molecular weight and colloidal forms of trace metals from smaller species. The discrimination between the colloidal forms of trace metals and the smaller “dissolved” species is arbitrary (Apte and Batley, 1995), for example, filtration through a 0.45- μm or 0.20- μm pore-size membrane filter. Peepers are designed to measure concentrations of dissolved components in interstitial (when placed in sediment) and overlying waters (Hesslein, 1976).

The principle operation of the sampler is the equilibration of a contained quantity of deionized water with the surrounding water through a membrane (~2 days in aquatic environments; Davison *et al.*, 2000). After deployment, the water contained in the peepers is removed for analysis of total dissolved metal concentrations. There are two basic advantages in using peepers: the discrimination against molecules is dependent on the pore size of the membrane chosen, and the technique eliminates the need for post-deployment filtration (Hesslein, 1976).

All of the methods described above require a water sample to be collected from the field, and returned to the lab for analysis. This is a potential drawback because metal speciation can be affected by uncontrolled changes in temperature, pressure, pH, oxygen concentration and losses or adsorption to sampling equipment during sample collection, storage, or treatment (Buffle and Horvai, 2000). To prevent contamination of samples elaborate clean handing techniques are required (Nriagu *et al.*, 1993).

A relatively new technique, Diffusion Gradients in Thin-films (DGT) (Davison and Zhang, 1994), has the potential to measure the free-metal ion, without the drawbacks of the previously mentioned approaches to metal speciation. The DGT technique is a simple *in situ* device which measures the flux of metal ions through a hydrogel, backed by a metal complexing resin. Theoretically, the technique measures “labile” metal species; inorganic and organically complexed metals that dissociate as they diffuse through the hydrogel during the time required for diffusion. Providing the concentrations of complexants and the stability constants of all DGT-labile metal species are known, it is theoretically possible to calculate the free-ion activity from total labile metal species using speciation codes (e.g. WHAM) (Zhang and Davison, 2000). The technique has the potential to provide information on metal speciation in many environments such as: fresh and salt waters, soils and sediments.

The DGT approach to measure trace metal speciation in natural waters has many advantages over other techniques. The primary advantages are: the simplicity of the devices and ease of use, the ability to concentrate metals *in situ*, the low detection limits (capable of 4 pM), the capacity of measuring many metals simultaneously, and the application to different environments (Davison and Zhang, 1994, Zhang and Davison, 1995).

1.4. DGT THEORY

The DGT technique consists of a device that contains a Na cation-exchange resin embedded in a hydrogel (referred to herein as resin gel), that fixes metals rapidly and efficiently. The resin most commonly used in DGT devices is Chelex-100. Chelex-100 is a styrene divinylbenzene co-polymer containing paired iminodiacetate ions. The iminodiacetate act as chelating groups in binding polyvalent metal cations (BioRad, 2000). The selectivity of Chelex-100 resin for metal cations corresponds to that of iminodiacetate acid. It is dependent on the pH, ionic strength and presence of other complex forming species in a system (BioRad, 2000).

The resin gel is separated from the bulk (or deployment) solution by a well-defined diffusive layer, which consists of either a polyacrylamide or agarose hydrogel (referred to herein as hydrogel) that controls trace metal flux. Provided that the metal complexing capacity of the resin is not exceeded, the concentration at the resin surface is effectively maintained at zero throughout the deployment, creating a steep concentration gradient in the hydrogel layer (Fig. 1). Between the hydrogel and the bulk solution, a diffusive boundary layer (dbl) develops creating an area where transport of metal ions is by molecular diffusion. When deployed in natural waters, a 0.45- μm membrane covers the hydrogel to prevent the deposition of particles on the diffusion gel surface (Davison and Zhang, 1994, Zhang and Davison, 1995).

Theoretically the mass of metal fixed by the resin gel can be used to determine the concentration of labile metals in the bulk solution using Fick's 1st Law of Diffusion. The concentration of labile metal in the bulk solution (C_b ; mol·cm⁻³) can be determined by:

$$[C_b] = M_{DGT} \Delta g / {}^sD A t \quad (1)$$

where M_{DGT} is the mass of metal fixed by the resin gel (mol), Δg is the thickness (cm) of the hydrogel, sD is the diffusion coefficient (cm² s⁻¹) of the metal in the hydrogel, A is the area (cm²) of the hydrogel exposed to the bulk solution, and t is the duration of deployment (s) (Davison and Zhang, 1994).

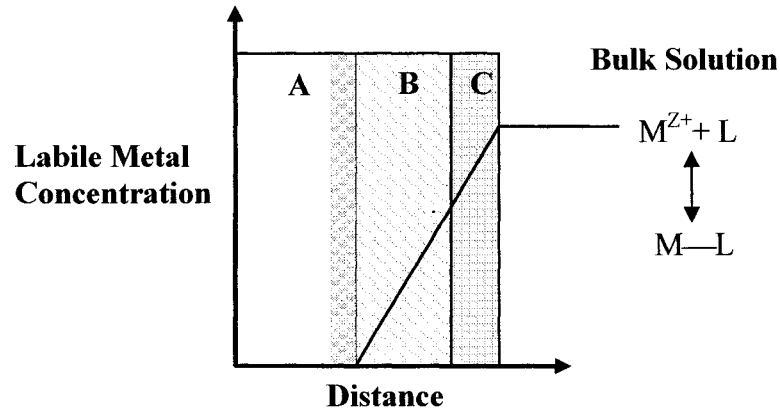


Figure 1. Concentration gradient of a metal ion in a DGT device. Where A, B, and C represent the resin gel, hydrogel and filter membrane respectively.

The mass of metal fixed by the resin gel (M_{DGT}) can be determined by elution of the resin gel with a known volume (V_e) of acid (e.g. 2 M HNO₃). The concentration of metal in the eluent can be measured by graphite furnace atomic absorption spectroscopy (GFAAS). It has been found (Davison and Zhang, 1994, Alfaro De-la Torre *et al.*, 2000) that only a fraction of the metal bound to the resin is eluted in the acid. The ratio of the eluted to bound metal is

termed the elution factor (f_e). The elution factor is used to determine the mass of metal ions fixed by the resin gel (M_{DGT} ; mol):

$$M_{DGT} = C_e(V_g + V_e)/f_e \quad (2)$$

where C_e is the concentration of metal in the eluent ($\text{mol}\cdot\text{cm}^{-3}$), V_g is the hydrogel volume (mL) in the resin layer and V_e is the volume of eluent (mL) (Zhang and Davison, 1994).

Diffusion coefficients of metals in the hydrogel (D) can be estimated using a diaphragm diffusion cell. The diaphragm diffusion cell has been recognized as the most accurate apparatus for measuring diffusion coefficients in hydrogels (Zhang and Davison, 1999). The diffusive layer thickness (Δg) is measured using a microscope and a micrometer, the area of the hydrogel exposed to the bulk solution (A) can be easily estimated from the area of the window in the DGT device, and the duration of deployment (D) can be measured with a chronometer.

In their work, Zhang and Davison (1995) assume that the diffusion coefficients of the metal ions in the hydrogel, filter and diffusive boundary layer equal the diffusion coefficient for that species in water at a given temperature; and that the thickness of the hydrogel is much greater than that of the filter and the diffusive boundary layer, and are therefore not included in the calculation.

The thickness of the diffusive boundary layer (dbl) can be estimated by rearranging equation 1 to:

$$1/M = \Delta g/DAt[C_b] \quad (3)$$

If we assume that the thickness of the hydrogel and filter is Δg , and the thickness of the diffusive boundary layer is represented by δ , equation 3 becomes an equation of a line:

$$1/M = \Delta g/DAt[C_b] + \delta/DAt[C_b] \quad (4)$$

such that by plotting $1/M$ versus the combined thickness of the hydrogel and filter, the thickness of the dbl (δ) can be estimated to be the negative value of the x-intercept.

1.4.1 Lability Distinction

Similar to voltammetry, DGT measures a flux, or the rate of supply to a given area in a given time. The rate of supply from solution depends on the kinetics of solution exchange, so the DGT measures a labile fraction of species in solution (Zhang and Davison, 1995). The lability of a metal ion is determined by the ability of its complexes to dissociate while diffusing through the hydrogel. Davison and Zhang (2000) assume that the resin binds exclusively with the free metal ion, so that measurement of a metal complex, $M-L$, only occurs if it can dissociate during the measurement time. The measurement time is related to the residence time (t ; s) of species in the hydrogel and can be estimated by

$$t = (\Delta g)^2 / 2^g D \quad (5)$$

where Δg is the hydrogel thickness (cm), and $^g D$ is the diffusion coefficient of the metal ion in the hydrogel. Using this method, inert complexes are not measured (Davison, 1978).

Therefore, the species measured by the DGT depends on the hydrogel thickness and their respective rate of diffusion through the hydrogel (Zhang and Davison, 1995)

1.4.2 Measurement of DGT-labile Species

According to Zhang and Davison, the pore size of the hydrogel can determine the species that diffuse through to be measured. By varying the composition of the hydrogels, the chemical species that pass through the hydrogel can be manipulated (Zhang and Davison, 2000).

In the polyacrylamide hydrogel, the concentration of acrylamide used determines the average length of the linear chains of polymer, and the concentration of bis-acrylamide

determines the extent of cross-linking (Dunn 1993). The effective pore size of the hydrogel is expressed as: the total concentration of acrylamide monomers plus cross-linking agent, and the concentration of the cross-linking agent alone. Hydrogel compositions are usually defined by using the parameters %T and %C where:

$$\%T = \text{acrylamide monomer} + \text{cross-linking agent \% (w/v)}$$

$$\%C = \text{the total monomer which is the cross-linking agent \% (w/w)}$$

Pore size is increased by a decrease in %T at a fixed %C, and as the proportion of cross-linker decreases (%C) at a fixed %T (Dunn 1993). The effective pore size decreases and reaches a minimum when the bis-acrylamide represents 5% of the total monomer. Further, hydrogels with values less than 2.5%T (very dilute) are unstable (Dunn, 1993 and Hames, 1981).

It is hypothesized that manipulating the composition of the hydrogels allows the use of DGT to discriminate between metal species according to their size and lability. Using hydrogels with large pore sizes (referred to herein as “open”) and small pore sizes (referred to herein as “tight”), it may be possible to determine DGT-labile “organic” and “inorganic” species in aquatic systems (Zhang and Davison, 2000). DGT-labile “inorganic” species refer to the free-metal ion and metal-inorganic complexes that dissociate during the measurement time. DGT-labile “organic” species are metal-organic complexes that are capable of dissociating during the measurement time.

According to Zhang and Davison, to measure both DGT-labile “inorganic” and “organic” metal species, a series of DGT devices with the two different hydrogel formulations must be deployed simultaneously in the same solution, for the same duration. The mass of metal measured by each DGT device (M_{DGT}) is the sum of both labile inorganic (M_{inorg}) and organic (M_{org}) species, and can be expressed as:

$$M_{DGT} = M_{inorg} + M_{org} \quad (6)$$

M_{inorg} and M_{org} can be represented by:

$$M_{inorg} = ({}^gD_{inorg} C_{inorg} At) / \Delta g \quad (7)$$

$$M_{org} = ({}^gD_{org} C_{org} At) / \Delta g \quad (8)$$

where ${}^gD_{inorg}$ and ${}^gD_{org}$ are the tracer diffusion coefficients of the inorganic and organic species and C_{inorg} and C_{org} are the DGT-labile “inorganic” and “organic” concentrations of trace metal measured by the DGT. Since the DGT devices used have the same geometric dimensions and are deployed for the same duration, equations 7 and 8 can be substituted into equation 6, and the mass fixed by the DGT can be represented as:

$$M_{DGT} = ({}^gD_{inorg} C_{inorg} + {}^gD_{org} C_{org}) At / \Delta g \quad (9)$$

the equation can be rearranged to:

$$M_{DGT} / [(At / \Delta g) {}^gD_{inorg}] = C_{inorg} + ({}^gD_{org} / {}^gD_{inorg}) C_{org} \quad (10)$$

where plotting $M_{DGT} / [(At / \Delta g) {}^gD_{inorg}]$ versus ${}^gD_{org} / {}^gD_{inorg}$ gives a straight line. Davison and Zhang (2000) hypothesize that the “open” hydrogel allows the almost free diffusion of simple metal ions and organic complexes and the “tight” hydrogel restricts the diffusion of most of the organic and inorganic species. By plotting $M_{DGT} / [(At / \Delta g) {}^gD_{inorg}]$ versus ${}^gD_{org} / {}^gD_{inorg}$ for the “open” and “tight” hydrogels on the same graph, the DGT-labile “organic” and “inorganic” trace metal concentrations can be determined, provided the ratios of ${}^gD_{org} / {}^gD_{inorg}$ are different between the two hydrogel types used. The y-intercept represents the concentration of DGT-labile “inorganic” species, while the slope represents the concentration of DGT-labile “organic” species (Zhang and Davison, 2000).

By using equation 10 to graphically solve for the DGT-labile “organic” and “inorganic” metal concentrations, Zhang and Davison (2000) make several assumptions:

1. the diffusion of the labile metal ion in the hydrogels equals that of the free ion (usually measured using a 0.01 M NaNO₃ solution in a diaphragm cell);
2. the diffusion of the metal-organic complexes in the hydrogels is equal to that of organic matter;
3. the diffusion of organic matter in natural water is equal to that of reference humic substances (e.g. Suwannee River Humic Substances).

1.4.3 Measurement of DGT-Labile “Inorganic” Species

Zhang and Davison propose (2000) that by deploying DGT devices fitted with “open” and “tight” hydrogels, measurements of the DGT-labile “organic” and “inorganic” concentrations of metal species can be determined, they also propose (2000) that the DGT devices deployed with “tight” hydrogels can be used for measuring DGT-labile “inorganic” concentrations directly. Zhang and Davison (2000) hypothesize that an estimate of DGT-labile “inorganic” metal species can be made using a “tight” hydrogel assuming that it can exclude DGT-labile and inert organic species (Zhang and Davison, 2000). Theoretically, the DGT-labile “inorganic” concentration can be determined by DGT devices fitted with “tight” hydrogels by omitting the ${}^{\text{D}}D_{\text{org}}C_{\text{org}}$ term in equation 9.

1.5. LABORATORY STUDIES

1.5.1 Development of the DGT Technique

Davison and Zhang (1994) found that the mass of metal accumulated by the resin gels was predicted quantitatively by equation 1 when DGT devices were deployed into two stirred solutions (0.5 M NaNO₃ and deionized water) spiked with 100 nM ZnNO₃. By deploying DGT devices for various times in adjusted solutions of natural sea water (pH range of 4.8-7.8), it was found that the mass accumulated by the resin gel increased linearly with time and the

concentration of labile Zn in the sea water sample agreed with concentrations measured by anodic stripping voltammetry (Davison and Zhang, 1994).

After deployment of DGT devices for 1 day, Zhang and Davison (1995) also determined that DGT devices have a concentration factor of approximately 300, allowing for the measurement of metals at extremely low levels (e.g. 4 pM). Also tested was the effect of temperature and ionic strength on DGT performance. To test the effect of temperature, DGT devices were deployed in solutions with temperatures ranging from 5 to 35 °C. Good agreement was found between experimental data and theoretical predictions, indicating that DGT measurements can be made in aquatic environments with temperatures ranging from 5 to 35 °C provided that diffusion coefficients are corrected for temperature. To test the effect of ionic strength, DGT devices were deployed into solutions of different ionic strengths ($1 \cdot 10^{-9}$ M NaNO_3) spiked with CdCl_2 . Cd concentrations measured by DGT devices agreed well with concentrations measured by GFAAS, suggesting that DGT measurements can be made in aquatic environments of different ionic strengths (Zhang and Davison, 1995).

Since the discrimination of trace metal species and the accuracy of the measurement rely on a knowledge of diffusion coefficients of these chemical species in the hydrogels, Chang *et al.* (1998) and Zhang and Davison (1999) focused on the characterization of agarose and polyacrylamide hydrogels used in the DGT technique. They found that when the hydrogels were exposed to solutions of SrCl_2 or Cd for 24 hours the concentration of metal ions in the hydrogels differed from the concentration measured in the solution (Chang *et al.*, 1998, Zhang and Davison, 1999). It was found that conditioning of the hydrogels in an electrolyte solution was required to obtain precise and accurate diffusion coefficient results. Provided that

conditioning of the hydrogels was complete (approximately 4 hours), the duration of conditioning did not affect hydrogel performance (Zhang and Davison, 1999).

In summary, it was determined that: the mass of metal ions accumulated by the DGT device increases linearly; the DGT technique can be used in aquatic conditions under wide temperature ranges; and conditioning of the hydrogels with an electrolyte solution is required to obtain accurate diffusion coefficients. Although this work represented a major step forward in the ability to measure trace metals *in situ*, further questions arose regarding the efficacy of the DGT technique.

1.5.2 Effect of Solution Conditions on the Diffusion Coefficients in the Hydrogel

Alfaro-De la Torre *et al.* (2000) conducted more robust laboratory experiments to determine if the composition and speciation of the bulk solution had an effect on the diffusion coefficients of metal ions in the DGT device. DGT devices were deployed in discrete well-stirred volumes of either filtered Lake Tantaré or deionized water spiked with Cd for 168 hours. Samples were collected periodically to monitor Na, Ca, Mg and Cd concentrations in the bulk solutions. In addition, replicate DGT devices were deployed in either 0.01 M NaNO₃ or filtered Lake Tantaré water spiked with Cd, Cu and Ni for 1 hour. In the first experiment, the DGT devices exposed to Lake Tantaré water released more Na from the resin gel and took up less Cd from the bulk solution than the DGT devices exposed to deionized water. In the latter experiment, the DGT devices exposed to Lake Tantaré water accumulated more Cd and Ni than the DGT devices exposed to the 0.01 M NaNO₃ solution over the same time period. The results from these experiments demonstrated that diffusive transport of metal ions in the hydrogel of DGT devices is complex when deployed in Lake Tantaré water because the diffusion of metal ions is strongly affected by the concentration, concentration gradient,

diffusion coefficient, and electrical contributions of the co-diffusing of ions (Alfaro-De la Torre *et al.*, 2000). In order to address this issue, Alfaro-De la Torre *et al.* (2000) hypothesized that the co-diffusion of ions in the hydrogel, not taken into account in original DGT theory, was responsible for overestimating metal concentrations in waters with low cation concentrations ($\sum [\text{cations}] \leq 2 \times 10^{-4} \text{ M}$). Therefore, the effective diffusion coefficient (D_{eff}) of the metal ion as described by Tessier *et al.* (1994a) should be amended as follows to satisfy electroneutrality:

$$D_{i,\text{eff}} = D_i - D_i z_i C_i \left[\frac{\sum_{j=1}^n z_j D_j \left(\frac{dC_j/dx}{dC_i/dx} \right)}{\sum_{j=1}^n z_j^2 D_j C_j} \right] \quad (11)$$

where D_i and z_i are the tracer diffusion coefficients of ion "i" (metal ion of interest) and its charge, respectively, and dC_i/dx and dC_j/dx are concentration gradients of ions "i" and "j" (all other ions) across the hydrogel. The second term in the right-hand side of equation 11 is referred to as the columbic or electrical component of $D_{i,\text{eff}}$ (Tessier *et al.* 1994a). Alfaro-De la Torre (2000) concluded that the effective diffusion coefficient ($^{\text{e}}D_{\text{eff}}$) rather than the tracer diffusion coefficient ($^{\text{e}}D$) should be used in equation 11 to calculate metal concentrations measured by DGT.

1.5.3 Measurement of DGT-labile Organic Complexes by the DGT Device

In an attempt to ascertain the accuracy of the DGT technique, Twiss and Moffett (2002) conducted experiments to determine if strongly bound organic complexes are DGT-labile. Several laboratory experiments were conducted with natural organic ligands in coastal seawater and synthetic organic ligands added to open ocean water. Replicate DGT devices were deployed for two days in Vineyard Sound seawater and 3 days in Sargasso seawater

spiked with DTPA and Cu. The results from the Vineyard Sound experiments demonstrated that Cu complexed with organics diffused through the hydrogel and was complexed by the resin. The Sargasso seawater experiments confirmed that Cu-DTPA were in fact DGT-labile. As a result of their work, Twiss and Moffett (2002) concluded that the inorganic complexes and strongly bound organic complexes diffuse through the hydrogels and are measured by the DGT device, which was fully addressed in the original DGT theory.

1.5.4 Estimates of DGT-labile “Organic” and “Inorganic” Species

To test the ability of DGT devices to measure DGT-labile “inorganic” and “organic” fractions in aquatic environments, Zhang and Davison (2000) deployed duplicate DGT devices fitted with three different hydrogel porosities into 6 solutions containing 3 different concentrations of CuNO₃ (0.5 μM, 1 μM and 2 μM) and either 1 mg/L fulvic acid or 1 mg/L humic acid (Zhang and Davison, 2000). The mass of Cu accumulated by the DGT devices, and independently determined diffusion coefficients for Cu, fulvic acid, and humic acid were used to calculate the DGT-labile “organic” and “inorganic” fractions by plotting $M_{DGT}/[(At/\Delta g)^g D_{inorg}]$ versus $^g D_{org}/^g D_{inorg}$ from equation 10. Results were compared with measurements of total dissolved Cu, and WHAM. With the exception of the solutions containing 2 μM Cu, total DGT-labile concentrations agreed well with the total dissolved metal concentrations. The DGT devices overestimated the DGT-labile “organic” concentration in the solution with the highest concentration of Cu (2 μM CuNO₃), and underestimated the DGT-labile “organic” Cu in the solution with the low Cu concentration (0.5 μM CuNO₃ when compared with WHAM predictions (Zhang and Davison, 2000). From their studies, Zhang and Davison (2000) concluded that DGT devices equipped with multiple hydrogel porosities were capable of measuring *in situ* concentrations of labile organic and inorganic species.

1.5.5 Behaviour of Metals in the DGT Devices

Recently, extensive experiments have been conducted (Tessier and Goulet, unpubl.) on the behaviour of trace metals in DGT devices. The following factors were examined: the diffusion of metals in a filter membrane, the interaction of metals with hydrogels, and the effects of solute, pore size, ionic strength and pH on the diffusion coefficient of metals in the hydrogel.

1.5.6.1 Behaviour of Metals in the Filter Membrane

The diffusion of Cd in a filter membrane commonly used in DGT devices (Whatmann, cellulose nitrate) was examined. It was found that the diffusion of Cd increased with decreasing ionic strength, apparently becoming greater than its diffusion in water at low ionic strengths ($\leq 10^{-3}$ M) at pH 5.45. The behaviour of Cd was attributed to the presence of negative charges in the filter membrane. The negative charges in the membrane result from ionization, and must be neutralized by positive counter-ions. At low ionic strength, competition from other ions in solution is inefficient, therefore Cd^{2+} ions will participate as the counter-ions. The consequence of these findings is that the calibration of the diffusion of metal ions in the DGT devices would become complicated since diffusion in the filters is dependent on external solution composition (Tessier and Goulet, unpubl.).

1.5.6.2 Behaviour of Metals in Hydrogels

Three different hydrogels were tested in the experiments: polyacrylamide cross-linked with bis-acrylamide (Fye), polyacrylamide cross-linked with Acryl Aide[®] (APA), and agarose (AGE) of various formulations. To study the interaction of metals with the hydrogels, the distribution coefficients (K_d) of metals between the hydrogels and the dissolved phase were determined according to the equation:

$$K_d = {}^s[M]/{}^w[M] \quad (12)$$

where ${}^s[M]$ is the concentration of metals (Cu, Cd or Hg) in the hydrogel, and ${}^w[M]$ is the concentration of metal in the bulk solution. If there is no interaction between metals and the hydrogels, distribution coefficients equate to unity. Hydrogels were equilibrated in solutions containing Cu, Cd or Hg. After equilibration, it was determined that there are specific interactions of metals with the hydrogels, noted by distribution coefficients greater than unity for the three metals in the hydrogels (Tessier and Goulet, unpubl.).

To study the effect of solute and pore size on the behaviour of metals (and organics), the diffusion coefficients of tritiated water, Cd, fulvic acid, and humic acid were determined in the three hydrogel types of various formulations. It was determined that for a given solute and type of hydrogel, the diffusion coefficient decreases systematically with an increase in monomer and cross-linker concentration (decrease in pore size) (Tessier and Goulet, unpubl.).

To study the effect of pH and ionic strength on the diffusion coefficients of metal ions, the diffusion coefficients of metal ions in the different hydrogels APA, AGE and Fye) were measured at various acidities at a fixed ionic strength (10^{-4} M), and at various ionic strengths and a fixed pH (~ 5.45). In the Fye hydrogels, the diffusion coefficient of Cd increased in the low ionic strength solution (10^{-4} M), and as the pH increased (pH 8.7-8.9). The behaviour of the metal ions was attributed to the presence of functional groups in the hydrogels. At high pH, or low ionic strength, ionization of these functional groups is favoured, and interaction with Cd^{2+} is therefore favoured (Tessier and Goulet, unpubl.).

Tessier and Goulet (unpubl.) have identified the functional groups in the agarose hydrogel as carboxylic groups.

Since it was determined that the diffusion of metal ions in hydrogels and filter differs from that in water, Tessier and Goulet concluded that the relationship of $[C_b]$ and M_{DGT} is more complex than what is expressed in equation 1 (Tessier and Goulet, unpubl.). Since the diffusion coefficients of metal ions in water, hydrogel, and filter have been found to be unequal, the concentration of metals in the external solution ($[C_b]$: $\text{mol}\cdot\text{cm}^{-3}$) should be equated to:

$$[C_b] = (M_{DGT}/At)(\Delta g/^gD + \gamma/^fD + \delta/^wD) \quad (13)$$

where M_{DGT} is the mass of metal fixed by the resin gel (mol), A is the area (cm^2) of the hydrogel exposed to the bulk solution, t is the duration of deployment (s), Δg is the thickness of the hydrogel (cm), gD is the diffusion coefficient ($\text{cm}^2 \text{s}^{-1}$) of the metal in the hydrogel, γ is the thickness of the filter (cm), fD is diffusion coefficient of the metal in the filter ($\text{cm}^2 \text{s}^{-1}$), δ is the thickness of the diffusive boundary layer (cm), and wD is the diffusion coefficient of the metal in the diffusive boundary layer ($\text{cm}^2 \text{s}^{-1}$) (Tessier and Goulet, unpubl.).

1.6 FIELD APPLICATIONS OF THE DGT TECHNIQUE TO AQUATIC ENVIRONMENTS

There are several studies demonstrating the field application of the DGT technique, but few have compared the technique with others in freshwater environments.

1.6.1 Menai Straits, UK

Davison and Zhang deployed several DGT devices in sea water (Menai Straits, UK, 32‰ salinity) for various times (Davison and Zhang, 1994). They found that the mass of Zn accumulated over time by the DGT devices was linear; indicating that mass transport is dominated by the hydrogel thickness. In addition, the concentration of Zn in the deployment solution measured by the DGT technique was less than that measured by anodic stripping voltammetry. Based on these findings Davison and Zhang concluded (1994) that the DGT

technique measures only labile species, and excludes chemically inert organic species and large colloids.

1.6.2 Pieman River and Hopkins River Estuary, Australia

Denny and others (1999) deployed DGT devices in four rivers in Pieman River, Tasmania, and Hopkins River Estuary, Victoria. Concentrations of Cu and Cd measured by the DGT in the rivers of the Pieman River catchment ($\sum [\text{cations}] = 3.4 \times 10^{-4} \text{ M}$) were less than or equal to the dissolved metal concentrations measured. Measured DGT labile concentrations of Cd and Cu less than the total dissolved concentration were attributed to the complexation of metals by humic substances or the presence of colloidal material not measured by the DGT technique. In the Hopkins River Estuary, the DGT accurately portrayed a concentration-depth profile for labile Mn, demonstrating the utility of the DGT technique to determine metal speciation across redox boundaries in stratified estuarine systems (Denny *et al.*, 1999).

1.6.3 Greenhole Beck, UK

Zhang and Davison (2000) deployed DGT devices fitted with three different hydrogel porosities in Greenhole Beck for 35 hours. The mass of Cu accumulated by the DGT devices fitted with restricted (“tight”) hydrogels and the diffusion coefficient of Cu in those hydrogels was used to determine the DGT-labile “inorganic” concentration of Cu in the stream using equation 9 omitting the ${}^{\text{g}}\text{D}_{\text{org}}\text{C}_{\text{org}}$ term. These results were compared to those obtained plotting $\text{M}_{\text{DGT}}/[(\text{At}/\Delta\text{g}){}^{\text{g}}\text{D}_{\text{inorg}}]$ versus ${}^{\text{g}}\text{D}_{\text{org}}/{}^{\text{g}}\text{D}_{\text{inorg}}$ from equation 10 using DGT devices fitted with 3 different hydrogel porosities. The DGT-labile “inorganic” Cu concentration measured using “restricted” hydrogels overestimated the DGT-labile “inorganic” metal concentration by approximately 11% when compared with the three different hydrogel methods for determining

labile inorganic and organic Cu. In addition, the DGT devices underestimated the DGT-labile “inorganic” Cu concentration in the stream when compared with the results obtained using the chemical speciation model WHAM (Zhang and Davison, 2000). This study represents the first report of the use of hydrogels with differing composition (porosity) to determine the DGT labile organic and inorganic concentrations independent of computer speciation codes.

1.6.4 Lake Tantaré, Canada

Alfaro-De la Torre *et al.* (2000) deployed DGT devices and *in situ* dialysis samplers (peepers) simultaneously in Lake Tantaré ($\Sigma [\text{cations}] = 5.6 \times 10^{-5} \text{ M}$). The DGT devices and peepers were fixed at various depths on two occasions for approximately one week. The concentrations of Cd and Ni measured by the DGT technique were greater than the concentrations of these metals measured by the peepers on both occasions (Alfaro-De la Torre *et al.*, 2000). The overestimation of measured DGT-labile Cd and Ni concentrations was attributed to the formation of a steep negative concentration gradient of Na across the diffusive layer (hydrogel), and a small positive concentration gradient of cations, when DGT devices are deployed in softwater lakes with low cation concentrations ($\Sigma [\text{cations}] \leq 2 \times 10^{-4} \text{ M}$). When this occurs, the result is an increase in the effective diffusion coefficient of the metals entering the DGT devices and a decrease in the diffusion coefficient of the Na^+ to fulfill electroneutrality (Alfaro-De la Torre *et al.*, 2000). It was concluded that DGT devices with the Na form of Chelex resin cannot provide accurate estimates of the concentration of metals in waters with low cation concentrations. Alfaro-De la Torre *et al.* (2000) suggested that charging the Chelex-100 resin with Ca^{2+} ions may rectify the problem. In a Ca form of the resin gel, there would be less unbound Ca in the hydrogel because Ca is more strongly bound to Chelex than Na, thereby having a lower gradient than Na across the hydrogel.

1.6.5 Vineyard Sound, Cape Cod, Elizabeth River, and San Diego Harbor, USA

Twiss and Moffett (2002) deployed DGT devices for 1 to 4 days in 4 different catchments distinguished by their level of pollution; Vineyard Sound, MA (pristine); Cape Cod, MA (small seasonally active harbours); Elizabeth River, VA (polluted estuary); San Diego Harbor, CA (large polluted port). The water samples were also characterized independently using competitive ligand exchange-adsorptive cathodic stripping voltammetry (CLE-ACSV). This represented the first time the DGT technique was compared with an independent speciation technique in marine systems. Twiss and Moffett were able to determine the effective diffusion coefficient of the Cu-complexing ligands using CLE-ACSV in unison with DGT. It was found that 10-35% of the organically complexed Cu derived by CLE-ACSV was in fact DGT-labile, demonstrating that both inorganic and organic complexes diffuse through the hydrogel. From these results, Twiss and Moffett (2002) concluded that the DGT technique can provide useful information regarding temporal and spatial variability and can be used as a monitoring tool for tracking episodic events where Cu is released into receiving waters (for example, when dredging).

As noted by the numerous field investigations, the attractive features of the DGT technique led to its rapid application in the field before its complete development under laboratory conditions (Zhang and Davison, 1995). DGT devices have also been used to measure radiocesium and phosphorus in natural waters (Murdock *et al.*, 2001, Zhang *et al.*, 1998a). In addition, DGT devices have also been used to measure the *in situ* concentrations and fluxes of trace metals in the porewaters of sediments and soils (Zhang *et al.*, 1995, Zhang *et al.*, 1998b).

1.7 REVIEW OF CURRENT STATE OF DGT KNOWLEDGE

Based on the aforementioned research conducted with the DGT technique, the following observations can be made:

1. Strongly complexed organic-metal molecules are able to diffuse through the hydrogel and be fixed by the Chelex-100 resin in the DGT device (Twiss and Moffett, 2002).
2. By deploying DGT devices with two different hydrogel formulations (“open” and “tight”), estimated concentrations of DGT-labile “organic” and “inorganically” bound metals can be determined *in situ* (Zhang and Davison, 2000).
3. The diffusion coefficients of metal ions in the hydrogels differ from the diffusion coefficients of metal ions in water. The diffusion coefficients are dependent on and influenced by: hydrogel type, formulation of the hydrogel, metal speciation, and solution conditions such as pH and cation concentration (Tessier and Goulet, unpubl.).
4. When deploying DGT devices in freshwater lakes with low cation concentrations ($\sum [\text{cations}] \leq 2 \times 10^{-4} \text{ M}$), the Na-based DGT device has been found to overestimate labile metal concentrations (Alfaro-De la Torre *et al.*, 2000).

1.8 THESIS OBJECTIVES

Based on the current state of DGT knowledge, the following objectives were established to ascertain the ability of the DGT technique to measure labile trace metal concentrations in freshwater environments:

1. Of primary importance was to determine if DGT devices fitted with hydrogels of different porosities could measure organic and inorganic concentrations of trace metals in freshwaters. To test this, a field study was conducted in which DGT devices fitted with

hydrogels of differing porosities were deployed in three different lakes of varying cation concentration.

2. The second objective was to ascertain if DGT devices with a Ca form of the resin gel would accurately predict bulk solution labile metal concentrations under conditions of low cation concentrations ($\sum [\text{cations}] \leq 2 \times 10^{-4} \text{ M}$) as hypothesized by Alfaro-De la Torre *et al.* (2000). To evaluate this, a Ca form of the resin gel was designed. Controlled laboratory experiments were conducted in which DGT devices equipped with a Na form of the resin gel or a Ca-form of the resin gel were deployed in solutions of varying cation concentration (2×10^{-3} , 2×10^{-4} , and $2 \times 10^{-5} \text{ M}$).
3. The third objective was to determine if the DGT devices with the Ca form of the resin gel could accurately predict labile metal concentrations in freshwater lakes with low cation concentrations. To test this, an extension of the field investigation was conducted and DGT devices with a Ca form of the resin gel were deployed simultaneously with DGT devices with the Na form of the resin gel in three different lakes of varying cation concentration.

1.9 SCOPE OF STUDY

Three freshwater lakes: Lake Tantaré, Lake St. Joseph, and Lake Memphremagog, were chosen for the field investigations. These lakes were selected because they have chemistries (pH, cation concentrations and DOC) representative of those found in the Canadian environment. These lakes are far from mining activities, therefore metal concentrations in the lakes are influenced by local weathering processes, domestic sources (cottages on Lake St. Joseph and Lake Memphremagog), and long-range atmospheric transport (Hare and Tessier, 1998).

The trace metals chosen for the study were Cd, Pb and Mn. Cd and Pb are both non-essential metals which have been found toxic to aquatic organisms at elevated concentrations (e.g. Borgmann et al., 1990, MacLean et al. 1996), and their toxicity has been found to be a function of metal speciation (Hare and Tessier, 1998). It is therefore important to determine the concentrations and speciation of these metals in the aquatic environment. The essential trace metal Mn was used as a reference metal, because its concentration in lakes is easily detectable by analytical techniques (GFAAS), and it is not readily complexed by organics (Sunda, 1984).

1.10 HYPOTHESES

Based on the findings of the research conducted by Alfaro-De la Torre *et al.* (2000) the following hypotheses are proposed to explain DGT function:

1. The DGT devices (Na-based resin gel) will provide reasonable measurements of the DGT-labile “organic” and “inorganic” concentrations of Mn, Cd and Pb in Lake Memphremagog ($\Sigma [\text{cations}] = 6.58 \times 10^{-4} \text{ M}$), as recognized by total DGT-labile concentrations less than or equal to the total dissolved concentration measured by *in situ* dialysis. The DGT devices in their Na form will overestimate these concentrations in Lake Tantaré and Lake St. Joseph ($\Sigma [\text{cations}] 5.79 \times 10^{-5} \text{ M}$ and $1.30 \times 10^{-4} \text{ M}$ respectively), as recognized by measured total DGT-labile concentrations greater than the measured total dissolved concentration.
2. In the laboratory experiments, the diffusion coefficients of metals entering the DGT devices with the Na-based resin gel will significantly increase under conditions of low cation concentration ($2 \times 10^{-5} \text{ M}$). In addition, the diffusion of metals entering the DGT with Ca-based resin gel will not increase under conditions of low cation concentration ($2 \times 10^{-5} \text{ M}$),

because Ca is much more strongly bound to Chelex than Na (Ca: 0.013 versus Na: 0.0000001, as compared to the affinity of Zn^{2+} for Chelex 100; BioRad, 2000),

3. The DGT devices equipped with the Ca-based resin gel will provide a reasonable measurement of the DGT-labile concentrations of Mn, Cd, and Pb in Lakes Tantaré and St. Joseph, due of the lower concentration gradient of Ca^{2+} (than Na^+) across the diffusive layer.

1.11 OUTLINE OF THESIS

Chapter 2 describes the methods that were common in all of the experiments in Chapters 3 to 5.

Chapter 3 summarizes the diffusion coefficients of metal ions (Mn, Cd and Pb) and natural organic matter determined for “open” and “tight” hydrogels in solutions representative of each lake. The diffusion coefficients calculated in these hydrogels will be used to calculate the DGT-labile “organic” and “inorganic” concentrations of metals in Chapter 5.

In Chapter 4, a Ca form of the resin gel is developed. The performance of Ca and Na forms of the resin gel in conditions of varying cation concentration are evaluated under controlled laboratory conditions. The premise that the diffusion coefficients of metal ions will increase under conditions of low cation concentrations is tested for DGT devices containing the Na form of the resin gel. In addition, the hypothesis that the diffusion coefficients of metals in DGT devices with the Ca form of the resin gel will not increase, is also tested.

In Chapter 5, the ability of DGT devices equipped with hydrogels of different porosities to measure DGT-labile “organic” and “inorganic” concentrations of Mn, Cd and Pb in freshwater lakes of differing cation concentration (Lake Tantaré, Lake St. Joseph and Lake Memphremagog) is assessed. The ability of the technique to measure DGT-labile “inorganic”

concentrations using a restricted hydrogel is also examined. In addition, an extension of the laboratory experiment is conducted in the field, and the ability of Ca-based DGT devices to accurately measure labile metal concentrations is studied *in situ*.

Chapters 3, 4, and 5 are written as complete experiments. Therefore concepts and techniques are repeated in the introductions, methods, and discussions in these chapters.

Chapter 6 summarizes the results and conclusions from the previous chapters (3-5), and critically examines and evaluates the ability of the technique for measuring labile trace metal concentrations in freshwater environments.

CHAPTER 2: STANDARD METHODS

The methods outlined in the following sections were used throughout the experiments described in the following chapters and are outlined here for brevity.

2.1 WATER SYSTEM

Water can be a major source of contamination in solutions (Nriagu *et al.*, 1993), and therefore ultrapure water was used when preparing all solutions and cleaning of apparatus. Ultrapure water used for experiments was derived from a multi-stage purification process. In the first stage, tap water was fed through a coarse filter (Rainfresh; Richmond Hill, ON) designed to remove large particles, slime, rust and loose scaling. After passing through the filter, the water was fed into a RiOs[®] system (Millipore Corp.; Bedford, Mass.). The RiOs[®] system is designed to remove particles and free chlorine from the water before being pressurized with a pump and purified by reverse osmosis (Millipore Corp, 1997). After the water was treated by reverse osmosis it entered the Milli-Q[®] system, and was pumped through a Q-guard[®] cartridge for an initial purification step. The water is then exposed to ultraviolet light at wavelengths of 185-254 nm to oxidize organic compounds. The water was then filtered through the Quantum[®] cartridge to remove trace ions and by-products of oxidation. The purified water passed through an ultrafiltration module that acted as a barrier to colloids, particles and organic molecules (molecular weight > 5000 Daltons). The point of use (POU) device contained a Millipack-40 membrane filter (> 0.22 μm) which prevented recontamination of the system from the POU device (Millipore Corp, 1997).

2.2 TRACE-METAL CLEAN TECHNIQUE

Preparation of solutions and manipulations were carried out in the Ryerson University Trace Metal Clean Laboratory.

All labware and devices were acid washed (see section 2.2.1) and handled with Class 1.5 compatible clean room gloves (Oak Technical; Stow, Ohio) to prevent contamination. Acid-clean plastic sheets were placed on counter tops when surfaces for manipulations were required.

2.3 WASHING PROCEDURES

2.3.1 Metals

All labware and devices that were to be free of metal contaminants were cleaned with dilute acid. Labware and devices were soaked in a plastic bath containing 1-3 % by volume Trace Metal Grade HCl (Fisher Scientific; Ottawa, ON) for at least 24 hours. After soaking, the labware was rinsed seven times with copious amounts of deionized water and dried in a laminar flow hood.

2.3.2 Organics

Specific labware was specially cleaned to remove organics according to the procedures of Kaplan (1994). Amber bottles were heated at 550°C for two hours in a muffle furnace, after which they were rinsed several times with deionized water. Plastics (bottles, filtration apparatus and pipettes) were cleaned by soaking in 10% (5% for filtration apparatus) sodium persulfate (J. T. Baker Chemical Company; Phillipsburg, N.J) solution for 1 hour at 60°C, followed by a seven-fold rinse with deionized water. Amber bottles and plastics were placed in a laminar flow hood to dry.

2.4 PREPARATION OF TRACE-METAL CLEAN SOLUTIONS

To prepare trace-metal clean solutions, solutions were passed through a column of Chelex-100. The Chelex-100 (Bio-Rad; Hercules, CA) resin was prepared according to the

technique of Price *et al.* (1989) to reduce contamination from trace metals and organic ligands (Table 1).

Table 1. *Preparation of clean Na Chelex-100 (modified from Price et al., 1989).*

-
1. Soak 200 g of Chelex-100 resin in 1 L of methanol for three to four hours; rinse with 4 L of deionized water using a scintered glass funnel (use for all further rinsing).
 2. Soak overnight in 2 L of 1 M Trace Metal Grade HCl (Fisher Scientific; Ottawa, ON); rinse with 4 L of deionized water.
 3. Soak in 2 L of NH₄OH for 1 week, rinse with 4 L of deionized water.
 4. Let the resin soak in 0.1 M HCl for 10 minutes, rinse with 8 L of deionized water.
 5. Charge Chelex with 99.996% metal basis NaOH (Alfa Aesar; Ward Hill, MA), and titrate with HCl to a pH of 7.
 6. Store moist in an acid-clean sealed container.
-

A plastic column was packed with ~10 g of clean Na Chelex-100. A crimped pipette tip was fitted to the column to obtain a flow rate between 4 and 7 mL min⁻¹. The solutions were slowly added to the column, to ensure that the resin bed was not disturbed. One hundred milliliters of solution was passed through the column and discarded. The remaining trace-metal clean effluent was collected and stored in a Teflon[®] bottle.

2.5 FORMULATION OF HYDROGELS

Fye hydrogels (Twiss and Moffett, 2002), whose composition is acrylamide cross-linked with bis-acrylamide, were used as the diffusive layer for all experiments. These hydrogels were chosen because they have the advantage of being chemically inert and stable over a wide range of pH, temperature and ionic strength. The hydrogels are formed by the polymerization of monomers of acrylamide into long chains with monomers of a bi-functional cross-linking agent, N'N'-methylene bis-acrylamide (Hames 1981). In order to solve for the

concentration of DGT-labile “organic” and “inorganic” species using equation 10, both “open” and “tight” Fye hydrogels were used as the diffusive layer. The composition of the “open” hydrogel was 8% by volume monomer plus cross-linker, and 2.7% by weight cross-linker (8%T, 2.7%C), while the composition of the “tight” hydrogel was 30% by volume monomer plus cross-linker, and 5% by weight cross-linker (30%T, 5%C) for all experiments.

2.5.1 Stock Solution Preparation

“Tight” hydrogel stock solutions were made by quantitatively mixing 45.60 g of acrylamide and 2.40 g of bis-acrylamide to 120 mL of deionized water. The final concentration of the stock solution was 40%T, 5%C. “Open” hydrogel stock solutions were prepared by mixing 35.04 g of acrylamide and 0.96 g of bis-acrylamide to 120 mL of deionized water. The final concentration of the stock solution was 30%T, 2.7%C. The pre-gel stock solutions were mixed thoroughly, stored in polycarbonate flasks, and kept refrigerated before use.

2.5.2 Hydrogel Preparation

The “tight” hydrogels were prepared using 18.75 mL of 40%T, 5%C stock solution and adding 6.00 mL of deionized water. The “open” hydrogels were prepared by mixing 6.70 mL of 30%T, 2.7%C stock solution with 18.15 mL of deionized water. The solutions were degassed for 15 minutes to remove oxygen that inhibits the polymerization process (degassing also prevents bubbles from forming in the hydrogel and aids in reproducible polymerization rates; Hames, 1981). After degassing, 250 μ L of freshly prepared 10% ammonium persulfate (APS) and 10 μ L of N,N,N',N'-tetramethylethylenediamine (TEMED) catalyst were added and mixed thoroughly. Since APS is unstable (Hames, 1981) it was prepared just prior to use. The final composition of the “tight” and “open” hydrogels was 30%T, 5%C and 8%T, 2.7%C respectively. The resulting solutions were immediately cast between 2 acid-clean glass plates

separated with plastic spacers of defined thickness. Hydrogels were allowed to polymerize for 40 minutes at room temperature ($25 \pm 5^\circ \text{C}$). After polymerization, the hydrogels were cut with an acid-clean punch from the sheet of hydrogel formed. The hydrogels were soaked and stored in deionized water (changing the water 6-7 times) to allow for the release of excess TEMED and APS to the bathing solution.

All reagents used for preparing stock solutions and hydrogels were electrophoresis grade (Fisher Scientific; Ottawa, ON).

2.6 GRAPHITE FURNACE ATOMIC ABSORPTION SPECTROSCOPY TECHNIQUE

Metal concentrations were analyzed using a graphite furnace atomic absorption spectrophotometer (GFAAS; AA-800; Perkin Elmer). Hollow cathode lamps (HCL) were used for the analysis Mn and Cd, and an electrodeless discharge lamp (EDL) was used for the analysis of Pb. For calibration curves, metal standard solutions were prepared by serial dilution of atomic absorption spectroscopy standards (VWR Brand). The metal standard solutions were spiked with concentrated HNO_3 (Seastar; Sidney, BC) to improve constancy and match the matrix of the solution. Certified reference material SLRS-4 riverine water (National Research Council Canada) was used periodically to confirm GFAAS accuracy with manganese samples. Standard additions were performed to ensure that the sample matrices were not suppressing metal signals.

CHAPTER 3: BEHAVIOUR OF MN, CD, PB AND ORGANIC MATTER IN HYDROGELS

3.1 INTRODUCTION

From their studies, Zhang and Davison (2000) concluded that DGT devices that are equipped with hydrogels of two different porosities can provide quantitative measurements of both the DGT-labile “organic” and “inorganic” concentrations of metals present in aquatic environments using equation 10. To determine both the DGT-labile “inorganic” and “organic” species, the diffusion coefficients of inorganic metals (D_{in}) and metal-organic complexes (D_{org}) in the hydrogels are required. For these purposes, it is assumed that the value of D_{in} is equal to that of the free metal ion measured in a synthetic solution, and the value of D_{org} is equal to that of natural organic matter in natural waters (Davison and Zhang, 2000).

From their work, Tessier and Goulet (unpubl.) have determined that both the pH and ionic strength of the bulk solution influence the diffusion coefficients of metals in hydrogels. Therefore, it is necessary to determine the diffusion coefficients of Mn, Cd and Pb, in “open” and “tight” hydrogels in synthetic lakewater solutions with cation concentrations and pH representative of Lakes Tantaré, St. Joseph and Memphremagog.

Alternatively, the effect of pH and ionic strength on the diffusion coefficients of natural organic matter in hydrogels remains to be extensively tested in the laboratory. Therefore, in order to accurately predict both the DGT-labile “inorganic” and “organic” species of metals using equation 10, it was necessary to determine diffusion coefficients of the natural organic matter indigenous to Lakes Tantaré, St. Joseph and Memphremagog in the “open” and “tight” hydrogels.

Distribution coefficient (K_d) values were determined for each metal in water representing each lake in the “open” and “tight” hydrogels in order to determine the effect of

pH and cation concentration on the interaction of these metals with the functional groups present in the hydrogels. K_d values for organic species were also calculated for each lake, to determine the extent of interaction, if any, with the hydrogels.

The diffusion coefficient of Mn, Cd, Pb and natural organic matter in Lakes Tantaré, St. Joseph and Memphremagog determined from these experiments will be used to determine both the DGT-labile “organic” and “inorganic” concentrations in these lakes (Chapter 5).

A diaphragm diffusion cell (Fig. 2) was used for the measurement of diffusion coefficients in both “tight” and “open” hydrogels. These cells have been recommended as the most accurate apparatus for measuring diffusion coefficients in hydrogels (Zhang and Davison, 1999). The cell was comprised of two compartments (A and B), separated by a 3.5-cm diameter circular opening. A 5.0-cm diameter, 0.14-cm thick hydrogel was sandwiched between the compartment openings, and provided the only connection between the two compartments. Simultaneously, equal volumes of solution were poured into compartments A and B, where compartment A was the “source” (of organic matter or metals) and B was the “sink”. The water was continuously stirred using Teflon[®] stirrers (> 550 rpm) (Fig. 2) to thoroughly mix the water and reduce the diffusive boundary layer (dbl). The diffusion cell was allowed to equilibrate for at least 12 hours before the first measurements were made. Equilibration ensures preconditioning of the hydrogels and measurable concentrations in the sink compartment at the initial sampling time. Temperature and stirring rate were monitored throughout the experiment. Measurements of acidity in compartments were made at the beginning and the end of each experiment to ensure they were ± 0.20 pH units.

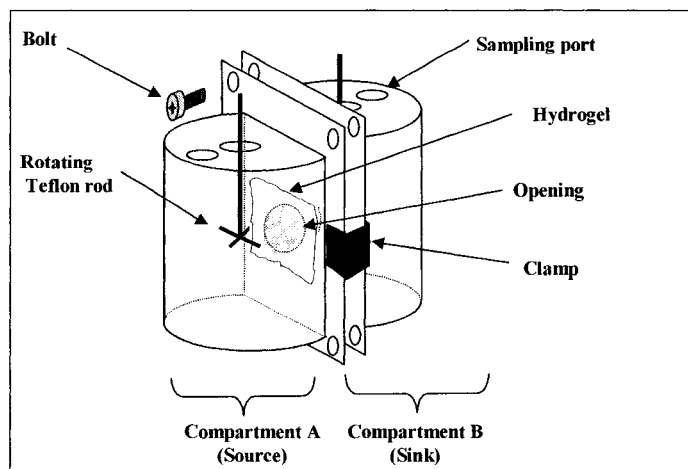


Figure 2. Schematic diagram of a diaphragm diffusion cell (diagram composed by Lise Rancourt).

The diffusion coefficient ($^{\circ}D$) of metals and organics in the hydrogels are governed by Fick's first law of diffusion (Zhang and Davison, 1999), and can be determined from the linear regression of mass (M ; mol) versus time (t ; s) in the sink cell according to:

$$M = ^{\circ}D(dC/\Delta g)At \quad (14)$$

where A is the area of the exposed hydrogel surface (cm^2), and $dC/\Delta g$ is the concentration gradient in the hydrogel (Zhang and Davison, 1999). The concentration gradient in the hydrogel is assumed to equal:

$$dC/\Delta g = ([C]_{\text{source}} - [C]_{\text{sink}})/\Delta g \quad (15)$$

where Δg is the hydrogel thickness and $([C]_{\text{source}} - [C]_{\text{sink}})$ is the difference in concentration (of organics or metals) in the source and sink compartments (Zhang and Davison, 1999).

Therefore, the diffusion coefficients of the metals in the hydrogels are calculated using:

$$M = ^{\circ}D\{([C]_{\text{source}} - [C]_{\text{sink}})/\Delta g\}At \quad (16)$$

Calculated diffusion coefficients are corrected for 25 °C using the following equation (Zhang and Davison, 1995):

$$\log D_T = \frac{1.37023(T - 25) + 8.36 \times 10^{-4}(T - 25)^2}{109 + T} + \log \frac{D_{25}(273 + T)}{298} \quad (17)$$

where D_T is the calculated diffusion coefficient at temperature T , and D_{25} is the corrected diffusion coefficient for 25°C.

3.2 METHODS

3.2.1 Formulation of Hydrogels

“Open” and “tight” hydrogels were prepared according to the procedure outlined in section 2.5.2. The hydrogels were cast at thicknesses of either 0.10 cm or 0.14 cm depending on the experiment.

3.2.2 Trace Metal Experiments

3.2.2.1 Solution Preparation

Synthetic solutions simulating the cation concentration and acidity of Lakes Tantaré, St. Joseph and Memphremagog were used for the metal diffusion coefficient experiments (Table 2).

To prepare the synthetic lakewater, three different stock solutions were made. The concentration of the major cations in Solution 1 was 48 mM CaCO_3 , 80 mM NaHCO_3 , 40 mM MgCO_3 , and 20 mM KCl . The acidity of the solution was adjusted to pH 2 by adding concentrated HCl . Stock Solution 2 was prepared by dissolving 0.712 g of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ in one litre of deionized water. The concentration of major cations in Solution 3 was 299 μM CaCO_3 , 135 μM NaHCO_3 , 93.5 μM MgCO_3 , and 20.5 μM KCl . The acidity of Solution 3 was adjusted to pH 2 by adding concentrated HCl .

Table 2. *Composition (major cation concentrations and pH) of Lakes Tantaré, St. Joseph and Memphremagog (Tessier, A., pers. comm.).*

Composition		Tantaré		St. Joseph		Memphremagog	
		Actual	Synthetic	Actual	Synthetic	Actual	Synthetic
Major Cations	Ca	21.9	22	56.7	56	379	379
	Na	22.4	20	46.2	55	165	175
	Mg	9.7	10.3	19.3	20	93.5	93.5
	K	3.9	5	7.4	10	20.5	20.5
	Total	57.9	57.3	129.6	141	658	668
pH		5.6	5.6 ± 0.1	6.4	6.4 ± 0.1	7.6	7.5 ± 0.2

Synthetic Lake Tantaré was prepared by quantitatively adding 0.250 mL of Solution 1 and 2.500 mL of Solution 2 per litre of deionized water. The resulting acidity and cation concentration was pH 5.6 (± 0.1) and 57.3 μM respectively (Table 2).

Synthetic Lake St. Joseph lakewater was prepared by quantitatively adding 0.500 mL of solution 1 and 7.750 mL of solution 2 per litre of deionized water. To adjust the acidity to pH 6.4 (± 0.1), 15 μL of 1 M NaOH was added per litre of solution. The resulting cation concentration was 141 μM (Table 2). Both synthetic lakewater solutions were stirred open overnight to equilibrate with the atmosphere.

Synthetic Lake Memphremagog was prepared by adding 2.5 mL of Solution 3 and 19.417 mL of Solution 2 per litre deionized water. To adjust the alkalinity to pH 7.6 (± 0.2), 175 μL of 1M NaOH was added per litre of solution. The calculated sum of the cations in the solution was 668 μM (Table 2). The solution was stirred open to the atmosphere for 6 hours.

3.2.2.2 Diffusion Experiments

Diffusion coefficients experiments for Mn, Cd, and Pb were conducted for Lake Tantaré, Mn and Cd for Lake St. Joseph and Lake Memphremagog.

Simultaneously, equal volumes of synthetic lakewater (175 mL) were transferred into each compartment of the diaphragm diffusion cell. After adding the synthetic lakewater, a

small volume (< 20 μL) of MnCl_2 , CdCl_2 or PbNO_3 was added to the source cell and was allowed to equilibrate for at least 12 hours. The initial concentration of metal added to the source compartment was 1 μM for each metal.

Due to the differing composition of the hydrogels, aliquots of 1 mL were taken every two hours for the “tight” hydrogel diffusion coefficient experiments and every hour for the “open” hydrogel diffusion coefficient experiments. The samples were analyzed for metal concentration by GFAAS.

3.2.2.3 K_d Experiments

The distribution coefficients (K_d) of metals between the hydrogels and the dissolved phase in purely inorganic media were determined according to the equation:

$$K_d = \frac{^g[\text{M}]}{^w[\text{M}]} \quad (12)$$

where $^g[\text{M}]$ is the concentration of metals (Mn, Cd or Pb) in the water present in the hydrogel, and $^w[\text{M}]$ is the concentration of metal (Mn, Cd or Pb) in the external (bulk) solution.

Using 0.10-cm thick and 25 mm-diameter “open” and “tight” hydrogels, K_d values for Mn, Cd and Pb were determined in Lake Tantaré, and Mn and Cd in Lakes St. Joseph and Memphremagog. The hydrogels were acclimated in triplicate for 24 hours in 15 mL of synthetic solutions of Tantaré, St. Joseph, or Memphremagog lakewater. After the acclimation period, each hydrogel was immersed into 14 mL of a metal spiked solution.

Lake Tantaré and Lake St. Joseph lakewater solutions were individually spiked with MnCl_2 , CdCl_2 or PbNO_3 to reach a final concentration of 10 μM . Lake Memphremagog was spiked with MnCl_2 , CdCl_2 or PbNO_3 to reach a final concentration of 1 μM . Samples (1 mL) were taken at the beginning and the end of the metal exposure period. After 24 hours, the hydrogels were removed from the metal solutions and extracted into 4.0 mL of 0.4 M HNO_3 .

For each metal, control experiments were conducted to determine the loss of metal from solution to the container. The control measured the disappearance of the metal from the solution over the duration of the experiment. In addition, process blanks were conducted with “open” and “tight” hydrogels. These hydrogels were not immersed into lakewater spiked with metals, but were acclimated and extracted using the same procedures. All samples were analyzed by GFAAS for metal concentrations.

3.2.2.4 Water Content of Hydrogels

The water content of 0.10-cm “open” and “tight” hydrogels was determined in order to calculate K_d . After the hydration period, a hydrogel was placed in a pre-weighed container and weighed. The container and hydrogel were dried in an oven at 60°C for 3 days then reweighed. This procedure was conducted in triplicate for both “open” and “tight” hydrogels. The water content of hydrogels was determined by calculating the difference between the dry weight and the wet weight of the hydrogels.

3.2.3 Organic Experiments

3.2.3.1 Water Sampling and Preparation

At the time of DGT retrieval, water samples were collected from Lakes Tantaré, St. Joseph and Memphremagog at the depth of DGT deployment for use in organic diffusion coefficient experiments. The water samples were kept dark in ice-packed coolers for transportation back to the laboratory (INRS-ETE, Université du Québec, Ste-Foy, QC). Lakewater samples were filtered through a 0.40- μ m membrane filter (Isopore; Millipore Corp, Bedford, MA). The samples were stored in dark amber glass bottles and kept refrigerated. A portion of the filtered water sample was irradiated in quartz tubes by exposure to ultraviolet light from a 1 kW Hg-vapour lamp to destroy organics. The duration of irradiation was

determined by a greater than 90% reduction in absorbance readings. The UV-irradiated samples then were refrigerated in plastic bottles.

3.2.3.2 Diffusion Experiments

Non-irradiated lakewater (150 mL) was poured into the source cell, and irradiated lakewater (150 mL) was simultaneously poured into the sink cell. Irradiating lakewater frees salts bound to organics, increasing the ionic strength of the irradiated water sample. Therefore, 150 μ L of 1 M NaCl was added to each compartment to equalize the ionic strength of both compartments to 10^{-3} M.

Aliquots of 30 mL were taken from each compartment every 2 hours for the “tight” hydrogel diffusion experiments and every hour for the “open” hydrogel diffusion experiments and measured by ultraviolet absorbance (Perkin Elmer, UV/VIS Lambda 20) at a wavelength of 326 nm in 10-cm pathlength quartz cells (Hellma; Richmond Hill, ON). After the measurements were taken, the samples were immediately returned to their appropriate compartments.

3.2.3.3 K_d Experiments

The distribution coefficient (K_d) for organics between the hydrogels and the dissolved phase was determined according to the equation:

$$K_d = \frac{^g[\text{Org}]}{^w[\text{Org}]} \quad (18)$$

where $^g[\text{Org}]$ is the concentration of fulvic acid in the water present in the hydrogel, and $^w[\text{Org}]$ is the concentration of fulvic acid present in the external (bulk) solution. The concentration of fulvic acid, $^g[\text{Org}]$, in the hydrogel is determined by:

$$^g[\text{Org}] = \Delta^w\text{Org}/^wV_g \quad (19)$$

where $\Delta^w\text{Org}$ is the change in mass of fulvic acid in the bulk solution, and wV_g is the volume of water present in the hydrogel. The change in mass of fulvic acid in the bulk solution is determined by:

$$\Delta^w\text{Org} = ^w\text{Org}_i - ^w\text{Org}_f \quad (20)$$

where $^w\text{Org}_i$ and $^w\text{Org}_f$ are the initial and final masses of fulvic acid in the bulk solution.

Using 0.10-cm thick, 25 mm-diameter “open” and “tight” hydrogels, K_d values for organics were determined for Lakes Tantaré, St. Joseph, and Memphremagog. Suwannee River Fulvic Acid (SRFA; International Humic Substances Society, USA) and synthetic lakewater solutions were used for the experiment since non-irradiated lakewater samples were not available. Synthetic lakewater for each lake was prepared as outlined in section 3.2.2.1, and the salinity was adjusted to 10^{-3} M NaCl to mimic the cation concentration used in the organic diffusion experiments.

The hydrogels were acclimated in triplicate for 24 hours in 50 mL of synthetic lakewater. After the acclimation period, each hydrogel was immersed into 50 mL of synthetic lakewater spiked with 7 mg/L SRFA for 24 hours. The initial absorbance of the three solutions was measured by ultraviolet absorbance (Lambda 20; Perkin Elmer) at a wavelength of 326 nm in 10-cm pathlength quartz cells (Hellma Canada, Concord, ON). Since the addition of SRFA to the solutions increased their acidity, the solutions were adjusted with NaOH to ensure they were within ± 0.2 units of their original pH. After 24 hours the hydrogels were removed, and the absorbance of each solution was measured.

3.3. RESULTS

3.3.1 Trace Metal Experiments

3.3.1.2 Diffusion Coefficient Experiments

Using equations 16 and 17 the mean apparent tracer diffusion coefficients (gD) of Mn, Cd and Pb were determined in the “open” and “tight” hydrogels, and are reported in Table 3.

The ratio of the diffusion coefficient in the hydrogel to that in water was computed ($^gD/^wD$; Table 3). These values can be compared to the “tortuosity” (Φ), of the hydrogels:

$$\Phi = ^gD_{\text{HTO}}/^wD_{\text{HTO}} \quad (21)$$

where $^gD_{\text{HTO}}$ is the apparent tracer diffusion coefficient of tritiated water (HTO) in the hydrogel (cm^2s^{-1}), and $^wD_{\text{HTO}}$ is the tracer diffusion coefficient HTO in water ($2.44 \pm 0.57 \times 10^{-5} \text{ cm}^2\text{s}^{-1}$; Wang *et al.*, 1953). Tessier and Goulet (unpubl.) determined the tortuosity of the “open” hydrogels and the “tight” hydrogels used in these experiments as 0.74 and 0.47, respectively. The ratio of the apparent tracer diffusion coefficient in the hydrogel to the tracer diffusion coefficient in water ($^gD/^wD$) of Mn, Cd and Pb can be compared to the tortuosity of the hydrogels because the diffusion of HTO is a function of the porosity of the hydrogels, and is independent of pH and ionic strength of the bulk solution, since it does not interact with the hydrogel (Tessier and Goulet, unpubl.).

For both the “open” and “tight” hydrogels, the ratio $^gD/^wD$ for Mn, Cd and Pb in Lake Tantaré are comparable to their tortuosity. The apparent tracer diffusion coefficients of Mn in the “open” and “tight” hydrogels for St. Joseph are slightly faster than those in Lake Tantaré, but the apparent tracer diffusion coefficient of Mn in the “open” hydrogels for Lake St. Joseph fell within the range (mean \pm standard deviation) of that in Lake Tantaré (Table 3). The mean apparent tracer diffusion coefficients of Cd in the hydrogels determined for Lake St. Joseph

were larger (faster) than those determined in Lake Tantaré, and the ratio $\frac{D}{D^w}$ was significantly greater than the tortuosity of the hydrogels (Table 3). The tracer diffusion coefficients of Mn and Cd in the hydrogels determined for Lake Memphremagog were smaller (slower) than those determined in Lakes Tantaré and St. Joseph, and the ratio $\frac{D}{D^w}$ was less than the tortuosity determined for those hydrogels in both instances (Table 3).

Table 3. Mean apparent tracer diffusion coefficients ($\times 10^{-6} \text{ cm}^2 \text{ s}^{-1} \pm \text{S.D.}$) of Mn, Cd and Pb in "open" and "tight" hydrogels for Lakes Tantaré, St. Joseph, and Memphremagog at 25 °C, where $a = 1$, $b = 2$, $c = 3$, and $d = 4$ replicates.

Hydrogel	Lake		Mn	Cd	Pb
open	Lake Tantaré	$\frac{D}{D^w}$	5.58 ± 0.50^c	5.49 ± 0.97^d	6.85 ± 0.65^c
		$\frac{D}{D^w}$	0.81	0.77	0.72
	St. Joseph	$\frac{D}{D^w}$	5.82^a	$(7.13 \pm 0.20^b)^*$	—
		$\frac{D}{D^w}$	0.85^a	0.99	—
	Memphremagog	$\frac{D}{D^w}$	4.65 ± 0.38^b	4.44 ± 0.45^b	—
		$\frac{D}{D^w}$	0.68	0.62	—
tight	Lake Tantaré	$\frac{D}{D^w}$	2.50 ± 0.25^b	3.77 ± 0.05^b	3.88 ± 0.50^c
		$\frac{D}{D^w}$	0.36	0.53	0.41
	St. Joseph	$\frac{D}{D^w}$	2.92 ± 0.16^b	$(4.33 \pm 0.08^b)^*$	—
		$\frac{D}{D^w}$	0.42	0.60	—
	Memphremagog	$\frac{D}{D^w}$	2.54 ± 0.04^b	2.53 ± 0.21^b	—
		$\frac{D}{D^w}$	0.37	0.35	—

Notes: D^w is the diffusion coefficient in water at 25°C (Li and Gregory, 1974).

* The diffusion coefficients of Cd in Lake St. Joseph have been interpreted as 5.76 and 2.89 ($\times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$) for the "open" and "tight" hydrogels, respectively (see text for explanation; section 3.4.1)

3.3.1.2 K_d Experiments

The distribution of metals between the hydrogels and the dissolved phase was determined using equation 12. The concentrations of metal in the bulk solutions were corrected for the concentration change in the control solutions. The metal concentration in the hydrogel extracts was corrected with the metal concentration measured in the blank extracts.

The K_d values for all metals in the different lakewater solutions were greater than unity, ranging from 1.2 to 1.8 (Table 4). The K_d values for Mn, Cd (and Pb for Lake Tantaré) were similar within each lake (Table 4). Also, the K_d values determined for Mn and Cd for the “open” and “tight” hydrogels were similar between Lakes Tantaré and St. Joseph, yet greater than those determined for Lake Memphremagog (Table 4).

Table 4. Mean K_d values (\pm S.D., $n = 3$) for Mn, Cd, and Pb in “open” and “tight” hydrogels for Lakes Tantaré, St. Joseph, and Memphremagog.

Lake	Hydrogel	Mn	Cd	Pb
Tantaré	open	1.6 ± 0.0	1.7 ± 0.0	1.6 ± 0.1
	tight	1.6 ± 0.1	1.7 ± 0.0	1.8 ± 0.0
St. Joseph	open	1.5 ± 0.0	1.4 ± 0.0	—
	tight	1.6 ± 0.0	1.7 ± 0.0	—
Memphremagog	open	1.2 ± 0.0	1.2 ± 0.0	—
	tight	1.3 ± 0.0	1.2 ± 0.0	—

3.3.1.3 Water Content of Hydrogels

The water content of 0.10-cm “open” hydrogels was determined to be 0.6108 mL, or 95.4 % of the total hydrogel volume. The “open” hydrogels contained approximately 1.1 times more water than the “tight” hydrogels (0.5423 mL) (Table 5).

Table 5. Mean water content of hydrogels (\pm S.D., $n = 3$).

Hydrogel	Water Content of Hydrogels	
	(mL)	%
open	0.6108 ± 0.0159	95.4
tight	0.5423 ± 0.0261	82.1

3.3.2 Organic Experiments

3.3.2.1 Organic Diffusion Coefficients

The mean apparent tracer diffusion coefficients of the natural organic matter in the “open” and “tight” hydrogels for Lakes Tantaré, St. Joseph and Memphremagog were calculated using equations 16 and 17, and are reported in Table 6.

The mean apparent tracer diffusion coefficients of organic matter in the “open” and “tight” hydrogels for Lake Tantaré were found to be considerably faster than those determined for Lakes St. Joseph and Memphremagog. The mean apparent tracer diffusion coefficients of organics in the “open” and “tight” hydrogels for Lakes St. Joseph and Memphremagog were similar, and their standard deviations fell within the range of their means (Table 6), suggesting that there may be no difference between the diffusion coefficients for the two lakewaters.

Table 6. Mean apparent tracer diffusion coefficients ($\times 10^{-6} \text{ cm}^2 \text{ s}^{-1} \pm \text{S.D.}$) of organics in “open” and “tight” hydrogels for Lakes Tantaré, St. Joseph, and Memphremagog at 25 °C, where $a = 1$, $b = 2$, $c = 3$, and $d = 4$ replicates.

Hydrogel	Lake		
	Tantaré	St. Joseph	Memphremagog
open	3.92 ± 0.35^b	2.60 ± 0.04^a	2.78 ± 0.11^c
tight	1.60 ± 0.20^c	1.09 ± 0.12^c	1.16 ± 0.09^d

3.3.2.2 K_d Experiments

The distribution of fulvic acid between hydrogels and the dissolved phase was determined using equation 18. The loss of fulvic acid in the control solutions over the course of the experiment was negligible in comparison to the initial concentration ($< 1\%$).

Similar to the distribution coefficients obtained for the metals, the fulvic acid K_d values were greater than unity, indicating interaction of fulvic acid with the hydrogels. In contrast to the K_d values obtained for metals, the average K_d values for the fulvic acid differed significantly depending on the lakewater composition (Table 7). The K_d values for Lake Tantaré were significantly greater than one, indicating considerable interaction of fulvic acid with the hydrogels. The K_d values for fulvic acid in the Lake Tantaré “open” hydrogels were 4-fold and 3-fold greater than the K_d values in Lake St. Joseph and Lake Memphremagog “open” hydrogels respectively (Table 7). In addition, the fulvic acid K_d value for Lake Tantaré in the “tight” hydrogels was approximately 2-fold greater than the values determined for Lake

St. Joseph and Lake Memphremagog in the “tight” hydrogels (Table 7). The K_d values for hydrogels in Lake Memphremagog were only slightly greater than those values obtained for Lake St. Joseph, and the standard deviations fell within the range of the means (Table 7), suggesting that there may be no difference between the fulvic acid K_d values for the two lakewaters.

Table 7. Mean fulvic acid K_d values (\pm S.D., $n = 3$) for “open” and “tight” hydrogels in Lakes Tantaré, St. Joseph, Memphremagog.

Hydrogel	Lake		
	Tantaré	St. Joseph	Memphremagog
open	4.8 ± 0.1	1.2 ± 0.2	1.6 ± 0.8
tight	3.9 ± 0.1	1.7 ± 0.1	2.1 ± 0.3

3.4. DISCUSSION

3.4.1 Behaviour of Metals in Hydrogels

The ratios of $^sD/^wD$ in Lakes Tantaré and St. Joseph were found to be greater than the ratio of $^sD/^wD$ determined for Lake Memphremagog, and close to the tortuosity of the hydrogels. It is expected that the diffusion coefficients of metal ions in the hydrogels depend not only on the pore size of the hydrogel but also the size of the diffusing ions (Tessier and Goulet, unpubl.). Since the diameter of the metal ions ($Pb > Cd > Mn$) is greater than HTO (0.2 nm: Wang *et al.*, 1953; White and Dorion 1961), the ratio of $^sD/^wD$ of the metal ions in the hydrogel should be less than the tortuosity for all systems. This is not the case. In Lake Memphremagog, the ratios of $^sD/^wD$ for Mn and Cd, were less than the tortuosity of the hydrogels as would be expected (Table 3), yet the ratios of $^sD/^wD$ for Mn and Cd increased in Lakes Tantaré and St. Joseph. The increase in diffusion coefficient of the metals correlated with a decrease in the cation concentration in the bulk solution. In Lake St. Joseph the ratios of $^sD/^wD$ for Mn were slightly faster than those determined in Lake Tantaré, but fell within the

range (mean \pm standard deviation) of those determined for Lake Tantaré. Yet, in Lake St. Joseph, the ratios of $^{\text{B}}\text{D}/^{\text{W}}\text{D}$ for Cd were significantly greater than those determined for Lake Tantaré. There may have been a correlation between an increase in diffusion coefficients and an increase in pH. The ratios of $^{\text{B}}\text{D}/^{\text{W}}\text{D}$ for Pb could not be compared because it was not measured in Lakes St. Joseph and Memphremagog, but the values of $^{\text{B}}\text{D}/^{\text{W}}\text{D}$ do agree with those determined for Mn and Cd in Lake Tantaré.

These findings agree with the results of Tessier and Goulet (unpubl.), who determined that the diffusion of a given metal increases as pH increases and ionic strength decreases. In the low cation concentrations of Lakes Tantaré and St. Joseph, pH may affect the diffusivity of the metal ions in the hydrogels, whereas in Lake Memphremagog the effect of the cation concentration on the diffusion of the metal species in the hydrogels is significant.

In the absence of interaction of metals with the hydrogels, the distribution coefficients (K_d values) would be expected to equal unity. Since the K_d values were greater than unity, interaction of metals with the hydrogels is present. Similar to the diffusion coefficients, the K_d values varied with the sum of cation concentration and pH in lakes. In general, the K_d values of Mn and Cd were similar in Lakes Tantaré and St. Joseph, and decreased with an increase in cation concentration in Lake Memphremagog. This correlated with ratios of $^{\text{B}}\text{D}/^{\text{W}}\text{D}$ of these metals in the hydrogels (with the exception of Cd in St. Joseph). The lower K_d values in Lake Memphremagog may be explained by the composition of the bulk solution. Cations in the bulk solution will compete with the metals (Mn and Cd) for binding sites present in the hydrogels. Binding sites in a polyacrylamide hydrogel may be present as the functional groups of the amide groups present in the hydrogels. Positively charged cations may co-ordinate with the lone pairs present in the functional groups (e.g. O and NH_3) of the amides. When the sum of

cations in the bulk solution is low, Mn and Cd will interact with the hydrogels because competition for binding sites from bulk solution cations is inefficient. Ca^{2+} ions have also been found to be more efficient than Na ions for reducing the interactions of metals with the hydrogels because they compete more efficiently with binding sites than Na (Tessier and Goulet, unpubl.). Therefore, it is expected that the K_d values of Mn and Cd in Lake Memphremagog would be lower than the values in Lakes Tantaré and St. Joseph because the sum of cations is considerably greater, and the concentration of Ca is twice as great as the concentration of Na in the bulk solution.

With the exception of the diffusion coefficients of Cd in Lake St. Joseph, the trends observed in the diffusion coefficient experiments correlate well with the trends observed in the K_d experiments. The K_d values for Cd in “open” and “tight” hydrogels were similar to those determined for Mn in the synthetic lakewaters (and Pb in Lake Tantaré), yet the behaviour of the diffusion coefficients differed in St. Joseph. The unexplainable fast apparent tracer diffusion coefficient of Cd in these hydrogels is considered an anomaly since its behaviour differs markedly from that of Mn in the same hydrogels. To determine the DGT-labile “organic” and “inorganic” Cd concentrations (Chapter 5), diffusion coefficients of 5.76 and $2.89 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ were interpolated from the ratio of Mn to Cd diffusion coefficients in the “open” and “tight” hydrogels in Lakes Tantaré and Memphremagog.

3.4.2 Behaviour of Organic Matter in Hydrogels

The mean apparent tracer diffusion coefficients of the natural organic matter in the “open” and “tight” hydrogels for Lake St. Joseph and Lake Memphremagog were similar to previously determined diffusion coefficients of SRFA in the same hydrogels (J.L. Stewart, unpubl.). Using similar methods, Stewart determined the mean apparent tracer diffusion

coefficients of SRFA in the “open” and “tight” hydrogels were $2.72 \pm 0.56 \times 10^{-6}$ and $1.03 \pm 0.27 \times 10^{-6} \text{ cm}^2\text{s}^{-1}$ respectively. This suggests that the diffusive properties of the natural organic matter in Lakes St. Joseph and Memphremagog are similar to a reference fulvic acid of aquatic origin. These findings agree with the hypothesis that fulvic acids comprise approximately 50% to 80% of natural organic matter in freshwaters (Buffle, 1988; Wilkinson, 1997).

In Lake Tantaré, the diffusion of the natural organic matter in the hydrogels was faster than those determined for Lakes St. Joseph, Memphremagog and the reference SRFA. Although extensive experiments have yet to be conducted on the effects of pH and ionic strength on the diffusion coefficients of organic species in the hydrogels, the difference in the diffusivities of the organics may be attributed to the effects of pH and cation concentrations in lakewater. At low pH, the acidic functional groups present within the organic molecule will become protonated, and their conformation will become more compact (Campbell *et al.*, 1997). The protonated organics in Lake Tantaré are expected to be smaller and thus more mobile in the hydrogel matrix.

Similar to the distribution coefficients obtained for metals, K_d values of fulvic acid were greater than unity signifying interaction of fulvic acid with functional groups present in the hydrogels. Interestingly, the K_d values in Lake St. Joseph and Lake Memphremagog were similar, and less than those determined for Lake Tantaré. The behavior of fulvic acid in the hydrogels is consistent with the measured apparent tracer diffusion coefficients of natural organic matter in the hydrogels, and thus may explain the fast diffusion coefficients of organics in Lake Tantaré. At low pH, the electrostatic repulsion between the organic matter and the hydrogel will decrease, and the possibility of hydrogen bonding is enhanced (Campbell *et al.*,

1997). This hydrogen bonding will occur between the protonated organics and the lone pairs of the oxygen group present in the amide groups of hydrogels. The trends observed in the diffusion coefficient experiments correspond well to the trends observed for the K_d experiments. The observed agreement among results justifies the use of fulvic acid in the K_d experiments, and suggests that the quality of the natural organic matter in Lake Tantaré used to determine the diffusion coefficients of organics is similar to that of SRFA. Analogous to the behaviour of the metal ions, these results propose that the composition of the bulk solution have an apparent effect on the diffusion coefficient of natural organic matter. Systematic experiments should be conducted to determine the effect of bulk solution cation concentration and pH on the behaviour of natural organic matter, in particular SRFA.

What is interesting is that the effect of solution conditions on the diffusion coefficients of the organic matter in the hydrogels does not correlate with the findings of Lead *et al.* (2000). Lead *et al.* (2000) found that the diffusion coefficients of SRFA in solution decreased slightly with an increase in the acidity of solution, due to the formation of dimer and trimers. They also found that the effect of ionic strength on the diffusion coefficient was either small or insignificant. The difference in behaviour of organics in the hydrogels and in solution, may be attributed to the influence of the functional groups present in the hydrogels on the diffusion coefficients of the organic matter. Since the effect of pH on the diffusion coefficient of SRFA in solution differs from the effect of pH on the diffusion coefficient observed in the hydrogel the need to individually characterize the diffusion coefficients of natural organic matter in the hydrogels is required when deploying DGT devices in lakes where the nature of organic matter is unknown.

3.4.3 Conclusion

When deploying DGT devices in different lakes, the finding of these experiments demonstrates the need to individually characterize the diffusion coefficients of metals and organic species in “open” and “tight” hydrogels in synthetic lakewater solutions with cation concentrations and acidity representative of each lake.

CHAPTER 4: THE EFFECT OF RESIN GEL FORMULATION AND BULK SOLUTION CATION CONCENTRATION ON THE EFFECTIVE DIFFUSION COEFFICIENTS OF MN, CD AND PB

4.1 INTRODUCTION

From the results of their study, Alfaro-De la Torre *et al.* (2000) hypothesized that DGT devices equipped with a Na form of resin gel could not provide quantitative measurements of the mass transport of metals in waters with very low cation concentrations ($\sum [\text{cations}] \leq 2 \times 10^{-4}$ M). Alfaro-De la Torre *et al.* (2000) proposed to modify the DGT devices to contain a Ca form of the resin gel, leading to a lower free Ca concentration (than Na) in the resin gel, and thus lower Ca gradients across the hydrogel. This is because Ca has a greater affinity to Chelex-100 resin than Na (Ca: 0.013 versus Na: 0.0000001, as compared to the affinity of Zn^{2+} to Chelex-100; Bio-Rad, 2000).

The purpose of the experiments here was to study the performance of DGT devices with the Na form of the Chelex resin (referred to herein as a Na-based DGT device) under varying conditions of cation concentration (2×10^{-3} , 2×10^{-4} , and 2×10^{-5} M) in a controlled laboratory environment. Accordingly, it was to be determined whether the diffusion of metals entering the Na-based DGT devices increased under conditions of low cation concentration ($\sum [\text{cations}] \leq 2 \times 10^{-4}$ M). In addition, the form of DGT device was modified by charging the resin gel with Ca ions (referred to herein as a Ca-based DGT device). The performance of Na-based DGT devices were compared to the Ca-based DGT devices under the same solution conditions (2×10^{-3} , 2×10^{-4} , and 2×10^{-5} M NaNO_3) to ascertain whether DGT devices with the Ca-based resin exhibited no significant increase in diffusion coefficients of the metal ions in the low cation solution (2×10^{-5} M NaNO_3). To determine if the composition of the bulk solution affects the diffusion coefficients of the metal ions in Na-based and Ca-based DGT

devices, Na-based DGT devices and Ca-based DGT devices were also deployed in a low Ca concentration solution of 2×10^{-5} M $\text{Ca}(\text{NO}_3)_2$.

Based on the research conducted by Alfaro-De la Torre *et al.* (2000), it is hypothesized that the diffusion coefficients of the metals entering the DGT device with the Na-based resin will significantly increase under conditions of low cation concentration (2×10^{-5} M), due to the formation of a steep negative concentration gradient of Na ions, and a small positive gradient of counter ions across the diffusive layer. The diffusion of metals entering the DGT device with a Ca-based resin will not increase under conditions of low cation concentration (2×10^{-5} M), because Ca has a greater affinity for Chelex-100 than Na, causing a lower Ca concentration gradient than a Na gradient across the diffusive layer, thereby weakening the electrical effects on the diffusion coefficients of the metals entering the DGT devices (Alfaro-De la Torre *et al.*, 2000). If this hypothesis holds true, the use of Ca-based DGT devices may provide an alternative to the Na-based DGT in natural waters with low cation concentrations ($\sum [\text{cations}] \leq 2 \times 10^{-4}$ M).

4.2 METHODS

4.2.1 Preparation of Resin Gels and Hydrogels

4.2.1.1 Hydrogel Formulation

“Tight” hydrogels were used for the experiments in which the DGT devices were deployed in solutions of NaNO_3 , whereas “open” hydrogels were used for the experiments in which the DGT devices were deployed in $\text{Ca}(\text{NO}_3)_2$. The hydrogels were prepared according to the procedures in section 2.5.2, and were cast at 3 thicknesses (0.04, 0.10, and 0.14-cm), depending on the experiment.

4.2.1.2 Na-based Resin Gels

Na-based resin gels were prepared by mixing 12.5 mL of the 40%T, 5%C stock solution, 10 mL of deionized water, and ~9.0 g of clean Na Chelex 100 (Table 1). The solution was degassed for 15 minutes, and then 250 μ L of 10% APS and 10 μ L of TEMED were added and mixed thoroughly. The resulting resin solution was cast between 2 glass plates separated by 0.10-cm plastic spacers. The plates were kept in a horizontal position to allow for a uniform resin bed to form. The resin hydrogel was allowed to polymerize for 45 minutes at room temperature ($25 \pm 5^\circ\text{C}$). After polymerization, the large resin gel that was formed was soaked in deionized water (exchanging the water at least 4 times) to allow for the release of excess reagents to the bathing solution.

4.2.1.3 Ca-based Resin Gels

Clean CaCl_2 , adjusted to pH 7 (with clean $\text{Ca}(\text{OH})_2$), was used to charge the Na-based resin gel with Ca ions. The Na-based resin gel was submerged into 300 mL of 2 M CaCl_2 (pH 7). After 6 hours, the solution was discarded and 300 mL of fresh 2 M CaCl_2 (pH 7) was added. This was repeated once more with 2 M CaCl_2 and twice with 1 M CaCl_2 over five days. The resin gel sheet was rinsed with deionized water several times.

The exchange of Na^+ ions in the resin layer for Ca^{2+} ions was monitored throughout the experiment, using the same method described above with resin gel discs. After each equilibration of the resin discs with the CaCl_2 solution, three resin discs were removed from the solution and extracted with 5 mL of 2M HNO_3 in 8-mL HDPE bottles. To determine the residual concentration in the resin gels over time, the eluates were analyzed for Na using GFAAS.

4.2.2 Experiments

4.2.2.1 Bulk Solution Composition

Na-based DGT devices were deployed in triplicate in 4 solutions: 2×10^{-3} M, 2×10^{-4} M, and 2×10^{-5} M NaNO_3 , and 2×10^{-5} M $\text{Ca}(\text{NO}_3)_2$. The same experiments were conducted with Ca-based DGT devices.

Solutions were prepared with either clean NaNO_3 or $\text{Ca}(\text{NO}_3)_2$ depending on the bulk solution composition of the experiment. In order to prevent a build up of excess Na ions in the deployment solution (diffusing from the resin gel into the bulk solution), the optimal deployment time and volume of the bulk solution was calculated. It was determined that a deployment time of 4 hours in 20 L of bulk solution was required to prevent significant accumulation of Na^+ ions in the bulk solution ($< 2\%$ in the 2×10^{-5} M NaNO_3 solution).

Bulk solution concentrations of 100 nM Mn, Cd, and Pb were used to ensure adequate flux of metals into the DGT device over the 4-hour deployment period. The solutions were spiked with NaNO_3 (or $\text{Ca}(\text{NO}_3)_2$ depending on the experiment) and the metals one hour before the experiment to allow for complete mixing. Aliquots of 4 mL were taken at the beginning of the experiment to verify bulk metal concentrations.

4.2.2.2 Determination of the Diffusive Layer

To reduce the diffusive boundary layer (dbl) the solutions were stirred constantly, at rates greater than 450 rpm. The stir plates were calibrated with a tachometer over a 24-hour period to ensure a constant stirring rate was maintained throughout the duration of the experiment. To calculate Δg , the dbl for the system was determined. Two replicate Na-based DGT devices with 3 different hydrogel thicknesses (0.04, 0.10, and 0.14-cm) were deployed for 4 hours in 20 L of solution spiked with 100 nM Mn. The dbl was determined by plotting the

mass of Mn (mol^{-1}) fixed by resin hydrogel versus the sum of the hydrogel and filter thicknesses. The x-intercept of the equation of a best fit line estimates the average dbl value over the period of deployment (4 hours).

4.2.2.3 Elution Efficiency

The efficiency of extracting Mn, Cd and Pb from the Na-based resin gel and the Ca-based resin gel in 5 mL of 2 M HNO_3 was determined using the equation:

$$f_e = C_e / C_s \quad (22)$$

Where, f_e is the elution factor, C_e is the mass of metals (Mn, Cd or Pb) in the extract, and C_s is the mass of metal (Mn, Cd or Pb) accumulated by the resin as determined from the loss of metal from the external solution throughout the experiment.

A 100 mL bulk solution containing 100 nM each of Mn, Cd, and Pb was prepared in a Teflon[®] bottle. One 4-mL sample was taken from the bulk solution to verify the metal concentrations. Three Na-based resin gels were added to the solution and placed on a shaker table for 3 days. After 3 days, the resin gels were removed and placed into 8-mL HDPE bottles and spiked with 2 M HNO_3 (Seastar; Sidney, BC) to give a final volume of 5 mL (volume of eluent and resin gel). A 4-mL sample was taken from the bulk solution to determine the amount of metal fixed by the resin. The same experiment was conducted with the Ca-based resin gels.

Process blanks were conducted with Na-based resin gels and Ca-based resin gels to determine background concentrations of Mn, Cd, and Pb in the resin gels. These resin gels were not immersed into the metal spiked solutions, but eluted using the same procedure. The concentration of metals in the eluates and solutions were analyzed using GFAAS.

4.2.2.4 Preparation and Deployment of Sampling Devices

The DGT devices used were the piston type (DGT Research Ltd; UK), as described by Zhang and Davison (1995)(Fig. 3). A circular piece of resin gel was cut with an acid-clean punch from the larger gel sheet. The resin gel was placed on top of the piston face with the side containing the resin beads facing upward. A hydrogel of the same diameter was placed on top of the resin gel followed by a 0.45- μ m HVLP membrane filter (Millipore Corp; Bedford MA). The filter protects the hydrogel against adherence of particles (Davison *et al.*, 2000). The filter membranes were soaked in dilute hydrochloric acid (1% v/v), and rinsed with copious volumes of deionized water before use. The layers were kept wet with deionized water during assembly to prevent air bubbles from forming between the layers. The assembly was fitted tightly to the piston with a 2-cm diameter widow cap to prevent the bulk solution from entering the resin gel. Plastic tweezers were used for all manipulations. For deployment, three replicate DGT devices were submerged (weighted to prevent floating) into the bulk solution.

Process blanks of DGT devices containing Ca-based and Na-based resin were performed. These blanks were kept in a plastic bag (Zip-lock; Glad) for the duration of the experiment. The background concentrations of trace metals in the extracts were used to correct the concentration extracted from the deployed probes. The temperature, pH, and the duration of deployment were recorded for each experiment (Table 8).

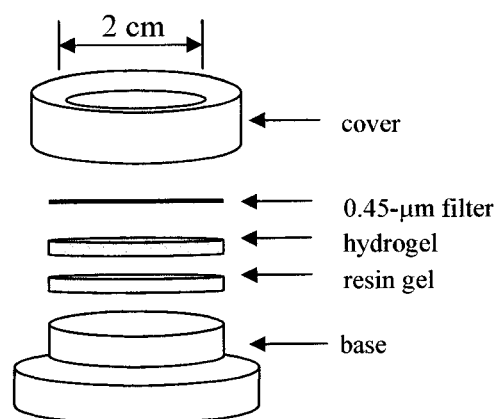


Figure 3. Schematic diagram of DGT device depicting location of base, resin gel, hydrogel, filter and window cap.

Upon retrieval from the bulk solutions, the devices were rinsed with copious volumes of water to stop metal diffusion. The devices were dismantled, and the overlying filters and hydrogel layer were removed and discarded. The resin gels were placed into 8-mL HDPE bottles. Accumulated metals were extracted in 5 mL of 2 M HNO₃ (Seastar; Sidney, BC), and analyzed by GFAAS.

Table 8. Experimental variables for the deployment of Na-based and Ca-based DGT devices in 20 L solutions.

Resin Gel	Solution	Duration of deployment (s)	pH	Temperature (°C)
Na-based	2×10^{-3} M NaNO ₃	14410	5.0	23
	2×10^{-4} M NaNO ₃	14409	5.0	23
	2×10^{-5} M NaNO ₃	14408	5.0	23
	2×10^{-5} M Ca(NO ₃) ₂	14400	5.0	19
Ca-based	2×10^{-3} M NaNO ₃	14401	5.0	23
	2×10^{-4} M NaNO ₃	14402	5.0	23
	2×10^{-5} M NaNO ₃	14406	5.0	23
	2×10^{-5} M Ca(NO ₃) ₂	14400	5.0	19

4.2.2.5 Calculation of Diffusion Coefficients

The diffusion coefficient ($^{\circ}D$; $\text{cm}^2 \cdot \text{s}^{-1}$) of the metal ions in the hydrogel was determined by rearranging equation 1 to:

$$^{\circ}D = M_{\text{DGT}} \Delta g / [C_b] A t \quad (23)$$

where M_{DGT} is the mass of metal flux into the probe (mol); Δg is the combined thicknesses of the hydrogel, membrane filter and the diffusive boundary layer (cm); $[C_b]$ is the concentration of metal in the bulk solution ($\text{mol} \cdot \text{cm}^{-3}$); A is the surface area of diffusion (cm^2); and t is the duration of deployment (s).

4.3. RESULTS

4.3.1 Determination of Residual Na in the Ca-based Resin Gels

Using equation 2 (assuming 100% extraction efficiency), the residual concentration of Na in a Ca-based resin gel was determined after each exchange. The initial concentration of Na in a Na-based resin gel was determined on the basis of Chelex-100 complexation capacity (Bio-Rad, 2000). The residual concentration in the Ca-based resin gel after 5 exchanges was determined to be $1.31 \mu\text{mol/g}$ Chelex-100, less than 1 % of the concentration in a Na-based resin gel (Table 9).

Table 9. Residual Na concentration ($\mu\text{mol/g}$ Chelex-100) in a Ca-based resin gel after 5 exchanges with CaCl_2 solution over a 5 day period.

number of CaCl_2 exchanges	Na Conc. ($\mu\text{mol/g}$ Chelex-100)	% residual Na
Na resin gel	615.38	100.0
1	50.47	8.2
2	8.45	1.4
3	2.41	0.4
4	1.34	0.2
5	1.31	0.2

The concentration of Na in the Ca resin gel decreased dramatically after the 1st exchange, and more gradually thereafter (Table 9). The concentration of Na in the Ca-based resin gel did not decrease significantly after the 4th exchange with CaCl₂ solution (Table 9), indicating that replacement of Na for Ca in the resin gel is complete after the 4th exchange of CaCl₂ solution.

4.3.2 Determination of the Diffusive Layer

The dbl was determined by plotting the inverse of the mass of Mn (mol⁻¹) fixed by resin hydrogel versus the sum of the hydrogel and filter thicknesses (Fig. 4). As previously mentioned the negative value of the x-intercept estimates the dbl thickness. A value of -0.0033 ± 0.0245 cm was the estimated dbl value. Since it is physically impossible for thicknesses to be negative, a dbl value of zero was adopted for the calculations. This is a reasonable assumption considering the fast stirring rate of the spinners (>450 rpm). By summing the thicknesses of the diffusive boundary layer (0.00 cm), hydrogel (0.10 cm) and filter (0.0125 cm), a diffusive layer (Δg) thickness of 0.1125 cm was used for the determination of the diffusion coefficients.

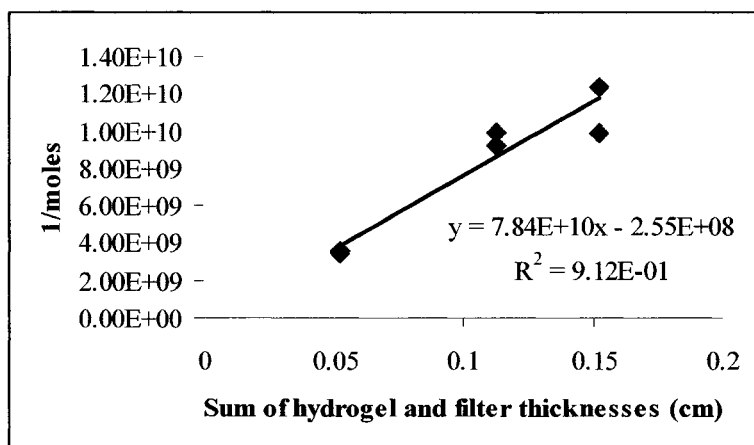


Figure 4. Graphical determination of the diffusive boundary layer (dbl) for a 20L carboy with a stirring rate greater than 450 rpm.

4.3.3 Elution Efficiency

The efficiency of eluting Mn, Cd and Pb from the Na-based resin gel and the Ca-based resin gel in 5 mL of 2 M HNO₃ was determined using equation 22. The metal concentration in the resin gel eluates was corrected for the metal concentration in the blank eluates.

Table 10. Mean elution factors for the efficiency of 5 mL of 2 M HNO₃ for eluting Mn, Cd, and Pb from Na-based resin gels and Ca-based resin gels ($n = 3$).

Resin gel	Mn	Cd	Pb
Na-based	0.91	0.84	0.96
Ca-based	0.87	0.72	0.83

The f_e values in the different resin gels differed between the different metal types and resin gel formulation (Table 10). The elution factor (f_e) was used to calculate the mass of metals fixed by the resin (M) of each DGT device using equation 2:

$$M_{DGT} = C_e (V_g + V_e)/f_e \quad (2)$$

where C_e is the concentration of metals in the extract, V_g is the volume of gel in the resin gel and V_e is the volume of eluent (Zhang and Davison, 1995).

4.3.4 Effect of Bulk Solution Cation Concentration on the Diffusion Coefficients of Mn, Cd and Pb

Overall, a net decrease in the diffusivity of the metal ions with decreasing cation concentration was observed in the DGT devices with the Na-based resin gel (Table 11). A decline of diffusion coefficients with decreasing cation concentration was observed for all 3 metals with the exception of Pb, in the 2×10^{-4} M NaNO₃ solution, where an increase in diffusivity was observed. The hypothesis that there was no significant decrease in the diffusion coefficients of Mn, Cd and Pb in the 2×10^{-5} M NaNO₃ compared to the 2×10^{-3} M NaNO₃ solution was tested using a Mann Whitney U test ($\alpha = 0.05$). If the diffusion coefficients for each metal in the two solutions were the same, they would be statistically

equal. Contrary to the hypothesis that the diffusion coefficients of metals ions entering the Na-based DGT will increase under conditions of low cation concentration, statistical analysis indicated that the diffusion coefficients of the Mn, Cd and Pb in the 2×10^{-3} M NaNO₃ solution were statistically faster than in the 2×10^{-5} M NaNO₃.

Table 11. Mean diffusion coefficients ($\times 10^{-6} \text{ cm}^2 \text{ s}^{-1} \pm \text{S.D.}$, $n=3$) of Mn, Cd, and Pb in DGT devices with 0.10-cm “tight” hydrogels deployed in solutions of different cation concentration (corrected to 25 °C).

Resin gel	Solution (M NaNO ₃)	Mn	Cd	Pb
Na-based	2×10^{-3}	3.46 ± 0.40	3.08 ± 0.18	0.50 ± 0.03
	2×10^{-4}	2.53 ± 0.10	2.48 ± 0.08	0.90 ± 0.82
	2×10^{-5}	2.27 ± 0.51	2.06 ± 0.48	2.39 ± 0.10
Ca-based	2×10^{-3}	3.03 ± 0.06	1.87 ± 0.24	0.42 ± 0.06
	2×10^{-4}	2.16 ± 0.03	1.50 ± 0.03	0.37 ± 0.29
	2×10^{-5}	3.59 ± 0.74	3.17 ± 0.71	0.98 ± 0.51

The behaviour of the diffusion coefficients of the metals entering the Ca-based DGT devices differed from that in the Na-based DGT devices. The decline in diffusion coefficients from the high cation concentration solution (2×10^{-3} M) to the low cation concentration solution (2×10^{-5} M) with the Na-based DGT devices was not observed with the Ca-based DGT devices. However, a decrease in the diffusion coefficients of metals was observed for all metals (Mn, Cd, and Pb) from the 2×10^{-3} M NaNO₃ to the 2×10^{-4} M NaNO₃, solutions. Yet, increases in the effective diffusion coefficients of Mn, Cd, and Pb, were observed in the low cation concentration solution (2×10^{-5} M) (Table 11). The hypothesis that no significant increase in the diffusion coefficients of Mn, Cd and Pb in the 2×10^{-5} M NaNO₃ compared to the 2×10^{-3} M NaNO₃ solution was tested using a Mann Whitney U test ($\alpha = 0.05$). If the diffusion coefficients for each metal in the two solutions were the same, they would be statistically equal. Contrary to the hypothesis that DGT devices with a Ca-based resin would express no significant increase in diffusion coefficients of metals ions in solutions of low

cation concentration, the results of the Mann Whitney U test indicated that the diffusion coefficients of the Cd and Pb in the 2×10^{-5} M NaNO₃ solution were statistically faster than in the 2×10^{-3} M NaNO₃ solution.

4.3.5 Comparison of Na-based and Ca-based Resin Gels

The average diffusion coefficients of Mn and Cd estimated using the Ca resin gels were slower than those determined using the Na resin gels in the 2×10^{-3} M and the 2×10^{-4} M NaNO₃ solutions (Table 2). The diffusion coefficient of Pb in the Ca-based DGT device fell within the range (mean \pm standard deviation) of those in the Na-based DGT devices in the 2×10^{-3} M and the 2×10^{-4} M NaNO₃ solutions, suggesting that there is no difference between the effective diffusion coefficients of Pb in the Ca and Na-based DGT devices in the 2×10^{-3} M and 2×10^{-4} M NaNO₃ solutions (Table 11).

By contrast, in the low cation concentration solution (2×10^{-5} M NaNO₃) the diffusion coefficients of Mn, Cd and Pb entering the Ca-based DGT devices were faster than the diffusion coefficients of the metals entering the Na-based DGT devices (Table 11).

The hypotheses that there was no significant difference between the diffusion coefficients of Mn, Cd and Pb in the Na-based and Ca-based DGT devices were tested using a Mann Whitney U test ($\alpha = 0.10$). If the diffusion coefficients for each metal in the Na-based and the Ca-based DGT devices were the same, then the average diffusion coefficients would be statistically equal. The results of the statistical analysis indicate that the diffusion coefficients of Mn, and Cd in the Ca-based DGT devices differed from those in the Na-based and Ca-based DGT devices. The diffusion coefficients of Pb in the Ca-based DGT devices differed from those in the Na-based DGT devices in the 2×10^{-5} M NaNO₃ solution, yet were statistically similar in the 2×10^{-3} M and 2×10^{-4} M NaNO₃ solutions.

4.3.6 Effect of the Compositions of the Bulk Solutions on the Performance of Na-based and Ca-based DGT Devices

Ca-based DGT devices and Na-based DGT devices were deployed in 2×10^{-5} M $\text{Ca}(\text{NO}_3)_2$ with 0.10-cm “open” hydrogels. In this experiment the behaviour of Mn, Cd and Pb in the Na-based and Ca-based DGT devices differed from the previous experiments in the 2×10^{-5} M NaNO_3 solution. In the low Ca solution (2×10^{-5} M $\text{Ca}(\text{NO}_3)_2$) the diffusion coefficients of Mn and Pb in the Ca-based DGT devices were slower than the diffusion coefficients in the Na-based DGT devices (Table 12). The diffusion coefficients of Cd cannot be compared because their standard deviations are greater than 95% of their mean diffusion coefficients.

Table 12. Mean diffusion coefficients ($\times 10^6 \text{ cm}^2 \text{ s}^{-1} \pm \text{S.D.}$, $n=3$) of Mn, Cd and Pb in 2×10^{-5} M $\text{Ca}(\text{NO}_3)_2$ in DGT devices with 0.10-cm “open” hydrogels (corrected to 25°C).

Resin	Mn	Cd	Pb
Na	7.36 ± 2.58	7.24 ± 7.07	10.74 ± 1.95
Ca	1.69 ± 0.08	$(36.2 \pm 29.2)^*$	1.93 ± 0.14

Note: *Value for Cd is not realistic due to different behaviour than Mn and Pb under the same conditions.

4.4 DISCUSSION

4.4.1 Effect of Cation Concentration on the diffusion coefficients of Mn, Cd, and Pb

The hypothesis that the diffusion coefficients of metals would increase with decreasing cation concentration was not observed with the Na-based DGT devices. In contrast, a decrease in the diffusivity of the metal ions with decreasing cation concentration was observed. With the exception of Pb in the 2×10^{-4} M Na NaNO_3 solution, the decrease in diffusion coefficient of the trace metals in the Na-based and Ca-based DGT devices was observed to correspond with the decrease in cation concentration of the bulk solution. This decrease in the diffusion coefficient may be attributed to the presence of functional groups in the hydrogel and the short deployment time. The trace metals in the bulk solution competed with Na for binding sites in

the hydrogel. In the solution with a high concentration of Na, many of the functional groups would become occupied with Na ions, and therefore allow the diffusion of Mn, Cd, and Pb in the hydrogel and become complexed by the resin. Since the duration of deployment was relatively short (4 hours), as the concentration of Na decreased in the bulk solution, more functional groups in the hydrogel became available as binding sites, and the interaction of these binding sites with Mn, Cd, and Pb increased as cation concentration decreased. The same may hold true for the decrease in diffusion of Mn, Cd and Pb in the Ca-based DGT devices in the 2×10^{-3} and 2×10^{-4} M NaNO_3 solutions. The increased diffusion of Pb in the 2×10^{-4} M NaNO_3 solution may be considered an anomaly since its behaviour differs significantly from that of Mn and Cd, and the standard deviation represents 91% of the mean value of the diffusion coefficient.

To remedy the problem, a longer deployment time may be used or the hydrogels may have to be preconditioned. Choosing a longer deployment time (1 day) may provide ample time for the functional groups present in the hydrogels to become saturated with Na ions and allow the diffusion of metal ions through the hydrogel, while only increasing the bulk Na concentration by approximately 7 %. Preconditioning the hydrogels in the same solution in which they will be deployed may also rectify the problem. After preconditioning, the functional groups in the hydrogels will become saturated with Na^+ or (Ca^{2+}) ions, and the Na (or Ca) concentration in the water portion of the hydrogels will be at equilibrium with that of the bulk solution, allowing the metal ions to diffuse through the hydrogels, and not associate with functional groups in the hydrogel.

The increase in the diffusion coefficients of Mn, Cd, and Pb in the Ca DGT device in the low cation solution (2×10^{-5} M NaNO_3) may be attributed to the binding efficiency of the

Ca^{2+} ions with the functional groups in the hydrogel at that particular cation concentration and pH. At low cation concentrations (2×10^{-5} M NaNO_3), there was a greater tendency for the cations to leave the resin gel in an attempt to maintain electroneutrality with the bulk solution. Since Ca^{2+} is a bivalent cation, it competes more efficiently than Na^+ ions for binding sites in the hydrogel, and therefore its capability of reducing the interactions of metals with the hydrogel is greater (Tessier and Goulet, unpubl.). Therefore, since more of the functional groups present in the hydrogels of the Ca-based DGT devices were occupied, the diffusion of the metals in the Ca-based DGT devices may have been faster than those in the solutions with a higher concentration of cations, and in the Na-based DGT devices.

The lack of increase in the diffusion coefficients of the metal ions in the Na-based DGT at low cation concentrations may signify that the DGT in the Na-resin form do not fail under conditions of low cation concentration as originally perceived. If the hydrogels were preconditioned in a solution with the same cation concentration as the bulk solution, the diffusion coefficients of the metals entering the DGT devices may not have decreased as observed in this study.

4.4.2 Comparison of Na-based and Ca-based DGT Devices

The slower diffusion coefficients of Mn, Cd and Pb in the Ca-based DGT devices in comparison to those in the Na-based DGT devices in these solutions may be attributed to the selectivity of Chelex resin for Ca. Ca is much more strongly bound to the Chelex 100 resin than Na (Ca: 0.013 versus Na: 0.0000001, as compared to the affinity of Zn^{2+} for Chelex-100; Bio-Rad, 2000), and there may be a lower Ca concentration gradient than Na^+ across the diffusive layer, weakening the electrical effects on the diffusion coefficients of the metals entering the DGT devices, as hypothesized by Alfaro-De la Torre *et al.* (2000). The diffusion

coefficients of Mn, Cd and Pb are faster in the Ca-based DGT devices in the low cation concentration solution because the Ca^{2+} ions in the resin gel compete more efficiently than Na ions for binding sites in the hydrogel as previously discussed.

The large error associated with the diffusion coefficients of the metals entering the Na-based DGT devices and Ca-based DGT devices in the low cation concentration solutions (2×10^{-5} M NaNO_3 and 2×10^{-5} M $\text{Ca}(\text{NO}_3)_2$) makes it difficult to draw any conclusions regarding the behaviour of the metal ions in DGT devices under these conditions. When hydrogels were preconditioned in deionized water Zhang and Davison (1999) found that the diffusion coefficient of Zn in hydrogels was 3.5% of the value of its free diffusion coefficient in water. After preconditioning the hydrogels in a solution of 0.1M NaNO_3 for 4 h the diffusion coefficient measured was the same as in water. Zhang and Davison (1999) concluded that preconditioning hydrogels was necessary to remove diffusional artifacts. Alternatively, the large error associated with the diffusion coefficients of the metals entering both the Na-based and the Ca-based DGT devices in the low cation concentration solution may also be attributed to the inherent inability of the technique to accurately measure labile metal concentrations in freshwater environments when $\sum [\text{cations}] \leq 2 \times 10^{-4}$ M.

4.4.3 Effect of the Composition of Bulk Solution on the Diffusion Coefficients of Mn, Cd and Pb

With the exception of Cd, the observed effective diffusion coefficients of the trace metals entering the Ca-based DGT devices were slower than those entering the Na-based DGT devices in the 2×10^{-5} M $\text{Ca}(\text{NO}_3)_2$ solution. The observed differences in the diffusion coefficients between the DGT devices may be attributed to the formulation of the bulk solution. To satisfy electroneutrality, the flux of Na (J_{Na^+}) out of the Na resin gel is described as:

$$J_{Na^+} = 2J_{Ca^{2+}} + 2J_{Mg^{2+}} + J_{H^+} + J_{K^+} + 2J_{\text{divalent trace metals}} \quad (24)$$

(Alfaro-De la Torre *et al.*, 2000). Since the flux of Mg and K is 0 (absent from solution), and the concentrations of H^+ and the trace metals (Mn, Pb, and Cd) is low (H^+ : 1×10^{-5} M, combined metal: 3×10^{-7} M) in comparison to that of Ca (2×10^{-5} M), the flux of Na out of the resin gel is effectively twice the flux of Ca into the resin gel (selectivity of Chelex for H^+ is low), and the resin gel has a greater affinity for Ca than Na. At low bulk Ca concentrations, the Ca^{2+} ions have a tendency to diffuse into the Na-based DGT devices. For every Ca^{2+} ion entering the resin, two Na^+ ions must leave, leading to an increased diffusivity of trace metals in order to maintain electroneutrality. In the Ca-based DGT devices, the flux of Ca^{2+} ions out of the resin is proportional to the flux of the ions into the resin. At low Ca concentrations there will be little tendency for the Ca^{2+} ions to diffuse into the resin gel. Therefore, the slower diffusion of metals into the Ca-based DGT devices in the 2×10^{-5} M $Ca(NO_3)_2$ solution may be attributed to the lack of co-diffusing ions in solution.

4.4.4 Reconciliation with Previous Studies

The findings from this study differ from those of Alfaro-De la Torre *et al.* (2000). In that study, seven Na-based DGT devices were deployed into 6 L of either filtered Lake Tantaré water ($\sum [\text{cations}] = 5.1 \times 10^{-5}$ M) or a 0.01 M $NaNO_3$ solution spiked with 17 nM Cd, and approximately 140 nM of Cu and Ni for 7 hours. DGT devices were retrieved at one hour intervals and the mass of metal fixed by the resin was measured. It was found that the effective diffusion coefficient of Cd in Lake Tantaré water was 1.98 times faster than the effective diffusion coefficient of Cd in 0.01 M $NaNO_3$ solution (Alfaro-De la Torre *et al.*, 2000). The increase in diffusion was attributed to the electrical contributions to the diffusion coefficient from the other cations in solution (Alfaro-De la Torre *et al.*, 2000). The differences

in our results with the Na-based DGT experiments may be attributed to the preconditioning steps of the hydrogels. Alfaro-De la Torre *et al.* report storing hydrogels in a 0.05 M NaNO₃ solution, after soaking, the water portion of the hydrogels will be at equilibrium with the external solution. A possible explanation for the increased diffusion coefficient of Cd into the DGT devices observed by Alfaro-De la Torre *et al.* may be due to the increased co-diffusion of Na ions out of the hydrogel into the bulk solution in an attempt to reach equilibrium with the bulk solution. The concentration of Na in the hydrogel was approximately 1000 times (0.05 M/0.00005 M) greater than the sum of cations in the filtered Lake Tantaré water, and only 5 (0.05 M/0.01 M) times greater than the cation concentration of the 0.01 M NaNO₃ solution. Therefore, the flux of Na out of the hydrogel would be much greater in the Lake Tantaré water than in the 0.01 M NaNO₃ solution, possibly increasing the diffusion of Cd into the DGT devices.

In order to incorporate effects of electroneutrality on the diffusion coefficients of metal ions, Alfaro-de la Torre *et al.* (2000) suggested that the effective diffusion coefficient of metal ions as described by Tessier *et al.* (1994a) should be used to calculate the concentration of metals in the bulk solution. Providing the concentrations and concentration gradients of all metals are known, the effective diffusion coefficients of Mn, Cd and Pb in the Na-based DGT device can be calculated using equation 11. Effective diffusion coefficients of $6.08 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$, $6.33 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$, and $8.35 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ were predicted for the low cation concentration solution ($2 \times 10^{-5} \text{ M NaNO}_3$) using equation 11 with the Na-based DGT devices (Appendix). The measured diffusion coefficients in the laboratory study in the same solution do not reconcile with these values: they are approximately 3-times less than those predicted for Mn, and Cd, and 33-times less than those predicted for Cd using equation 11. The

underestimation in the empirically determined diffusion coefficients may suggest one of the following: using equation 11 does not accurately predict the effects of electroneutrality on the diffusion coefficients of trace metals, or that preconditioning of the hydrogels is essential in order to obtain reproducible results.

4.4.5 Recommendations for Future Research

In an attempt to appropriately evaluate the Ca-based and Na-based DGT devices, the conclusions drawn from this study suggest that additional experiments should be conducted. Of primary importance is the repetition of these experiments with preconditioned hydrogels to determine if preconditioning has an effect on the effective diffusion coefficient of the metals under the condition used in this study. The hydrogel should be preconditioned in a solution with the same cation concentration as the deployment solution. Second, the experiments could also be conducted using different chemically defined media (synthetic lake waters) rather than varying concentrations NaNO_3 to determine the effect of various cations and their differing concentrations on the effective diffusion coefficients of the trace metals.

4.4.6 Conclusions

Based on these preliminary studies, the Na form of resin and the Ca form of the resin do not perform as theoretically predicted under conditions of low cation concentration. Although Ca-based DGT devices initially appeared to be an attractive alternative to Na-based DGT devices in waters with low cation concentration (Alfaro-De la Torre *et al.*, 2000), there are caveats (e.g. increased diffusion coefficients) associated with the Ca-based DGT devices that must be resolved before they can be used with confidence. In addition, more research on the performance of Na-based DGT devices in waters of varying cation concentration is also necessary before they too can be used with confidence in freshwaters.

CHAPTER 5: IN SITU DGT EXPERIMENTS

5.1 INTRODUCTION

From their studies Zhang and Davison (2000) concluded that DGT devices equipped with hydrogels of at least two different porosities can provide quantitative measurements of both the DGT-labile “organic” “inorganic” concentrations of metals present in aquatic environments using equation 10. In addition, they concluded that DGT devices fitted with a hydrogel of small pore size can provide a reasonable estimate of the DGT-labile “inorganic” metal concentration present in aquatic environments (Zhang and Davison, 2000).

From their results, Alfaro-De la Torre *et al.* (2000) concluded that DGT devices with the Na form of resin gel could not provide quantitative measurements of the mass transport of metals in freshwaters of very low cation concentration ($\sum [\text{cations}] \leq 2 \times 10^{-4} \text{ M}$). Alfaro-De la Torre *et al.* (2000) proposed to modify the DGT devices to contain a Ca form of resin gel.

The objective of this investigation was to deploy DGT devices with two different hydrogel porosities and measure the DGT-labile “organic” and “inorganic” concentrations of Mn, Cd, and Pb in freshwater environments. DGT devices fitted with “open” and “tight” hydrogels (section 2.5.2) were deployed in Lakes Tantaré, St. Joseph, and Memphremagog in Québec ($\sum [\text{cations}]$: Lake Tantaré < Lake St. Joseph << Lake Memphremagog; Table 2). The results were compared with the DGT-labile “inorganic” fraction determined using DGT devices fitted with “tight” hydrogels. Total dissolved metal concentrations ($< 0.20 \mu\text{m}$) measured using *in situ* dialysis samplers (peepers) were used to evaluate the results of the investigation.

In addition to the speciation studies, DGT devices with a Ca form of the resin gel (previously developed; refer to section 4.2.1.3) were deployed concurrently with the Na-based

DGT devices to compare their performance in the field. Accordingly, it was to be determined whether DGT devices equipped with a Ca-based resin provide a more reasonable measurement than Na-based DGT devices of total labile metal concentrations *in situ*. The concentrations DGT-labile “inorganic” Mn, Cd, and Pb determined using the Ca-based DGT devices were also compared to the total dissolved concentration measured by *in situ* dialysis.

Based on the research conducted by Alfaro-De la Torre (2000), it is hypothesized that the diffusion coefficients of the metals entering the DGT devices with the Na-based resin will significantly increase in Lakes Tantaré and St. Joseph, due to the formation of a steep negative concentration gradient of Na ions, and small positive gradients of counter ions across the diffusive layer. This increase in diffusion coefficients will overestimate the labile metal concentrations in Lake Tantaré and Lake St. Joseph. Therefore, the calculated total DGT-labile metal concentrations determined using the “open” and the “tight” hydrogels will overestimate the concentrations of metal in these lakes. For the same reason, the DGT-labile “inorganic” concentration of metals determined from the devices fitted with the “tight” hydrogels will also overestimate the metal concentration in the lakes, and will not provide a reasonable estimate of DGT-labile “inorganic” metal concentrations.

It is hypothesized that the diffusion coefficients of metals entering the DGT with the Ca-based resin will not increase in Lakes Tantaré and St. Joseph, because Ca has a greater affinity for Chelex than Na (Ca: 0.013 versus Na: 0.0000001, as compared to the selectivity for Zn; BioRad, 2000), and therefore the Ca-based DGT will provide a more reasonable estimate of labile metal concentrations in the lakes. If the hypothesis holds true, the use of Ca-based DGT devices rather than Na-based DGT devices may provide an alternative to the Na-based DGT devices in natural waters with low cation concentrations ($\sum [\text{cations}] \leq 2 \times 10^{-4} \text{ M}$).

5.2 METHODS

5.2.1 DGT Devices

5.2.1.1 Hydrogel and Resin Gel Formulation

“Open” and “tight” hydrogels were prepared according to procedures of section 2.5.2. The “open” hydrogels were cast at 0.10 cm; “tight” hydrogels were cast at 3 thicknesses (0.04, 0.10, and 0.14 cm).

Na-based resin gels were prepared according to the procedure outlined in section 4.2.1.2, and stored in deionized water until used. Ca-based resin hydrogels were prepared according to the procedures outlined in section 4.2.1.3, and stored in deionized water until used.

5.2.1.2 DGT Assembly

Mounting of the resin gel and hydrogel on the DGT holders followed the procedure outlined in section 4.2.2.4.

The DGT devices were secured in acrylic holders for *in situ* deployment. The holder consisted of two acrylic plates: back and front (Fig. 5). Holes fitting the diameter of the DGT caps were machined into the front plate. The back plate consisted of small holes over which 13 DGT devices were positioned (10 Na-based DGT devices and 3 Ca-based DGT devices). The plates were fastened together with plastic tie-wraps.

To keep the hydrogels and resin gels moist, the DGT units were moistened with approximately 2 mL of deionized water and sealed in plastic bags (Zip-Lock; Glad). The units were placed horizontally in an ice-packed cooler during transportation.

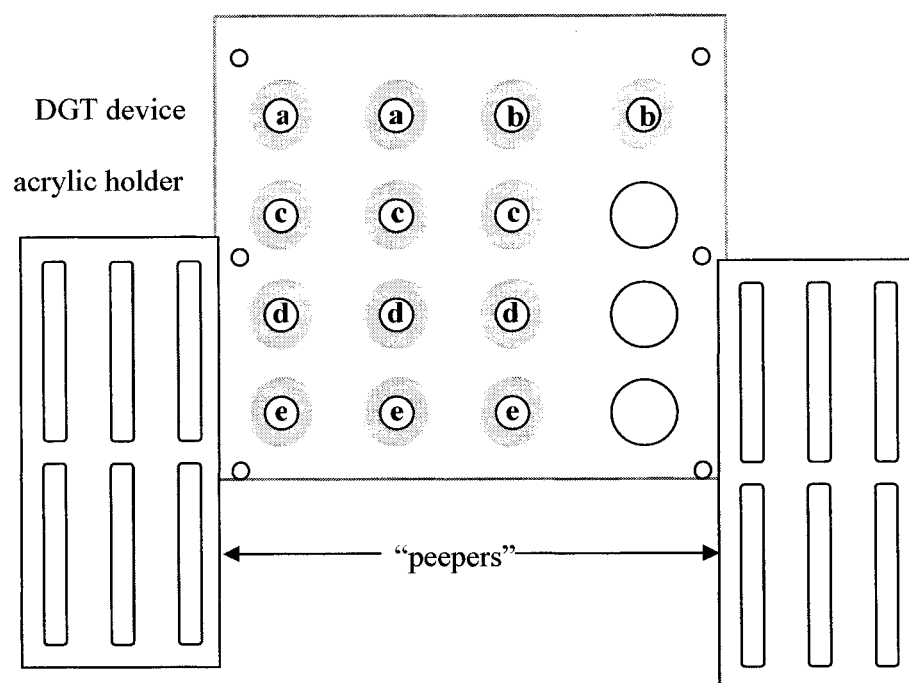


Figure 5. Diagram of DGT assembly, depicting location of the peepers and the DGT devices. Where a, b, and c represent Na-based DGT devices fitted with 0.04-cm, 0.14-cm, and 0.10 cm “tight” hydrogels respectively; d represents Na-based DGT devices fitted with 0.10-cm “open” hydrogels; and e represents Ca-based DGT devices fitted with 0.10-cm “tight” hydrogels. The dbf was determined using Na-based DGT devices with subscripts a, b, and c. Na-based DGT devices with subscripts c and d were used to determine both the DGT-labile “organic” and “inorganic” concentrations of metals. DGT-labile “inorganic” concentrations of metals were determined using the Na-based and Ca-based DGT devices with subscripts c and e.

5.2.1.3 Determination of the Diffusive Layer

To calculate the diffusive layer (Δg), the diffusive boundary layer (dbf) must be determined. Replicate Na-based DGT devices with “tight” hydrogels of 3 different thicknesses (0.04, 0.10, and 0.14 cm) were deployed at each location. The average dbf over the duration of deployment is determined by plotting $1/M$, where M is the mass in moles of Mn fixed by the resin, versus the sum of hydrogel and filter thicknesses. The x-intercept estimates the mean dbf value over the duration of deployment. By summing the thicknesses of the dbf, hydrogel and filter, specific Δg values can be calculated for the DGT device in each lake.

5.2.2 *In Situ* Dialysis

In situ dialysis samplers (peepers) were prepared and assembled at the INRS-ETE, following the procedure of Carignan *et al.* (1985). These samplers were similar in design to those described by Alfaro-De la Torre *et al.* (2000). The peepers consisted of a 21.6 cm x 7.2 cm x 1.2 cm acrylic sheet comprised of eight cells, each with a window area of 5.4 cm². The cells of the peepers were filled with 4 mL of deionized water and covered with a 0.2- μ m polysulfone membrane (HT-200; Gelmann). The membrane was adhered using an acrylic sheet with apertures matching the chambers. The peepers were stored in vacuum-packed plastic bags and kept horizontal for their transportation to the field.

5.2.3 Field Deployments of DGT devices and *In Situ* Dialysis Samplers

DGT devices and *in situ* dialysis samplers (peepers) were deployed simultaneously for a period of 7 days during August 2001 in the water column of Lakes Tantaré, St. Joseph, and Memphremagog in Quebec. Thirteen DGT devices (9 Na-based DGT devices and 3 Ca-based DGT devices) and two peepers were deployed at each location. Just prior to deployment, one peeper was attached to each side of the DGT unit with a plastic tie wrap (Fig. 5).

On August 1, 2001, at 10h30 the entire assembly (DGT devices and peepers) was deployed in the south central portion of Lake Tantaré (47°04'N, 71°32'W). The water depth at this location was 3.5 m. The assembly was fastened to a weighted monofilament nylon line that was pre-calibrated for depth and suspended in the water column 0.5 m from the sediment. A white plastic buoy was attached to the end of the line as a marker and to keep the assembly afloat. To protect the assembly, the buoy was partially filled with water to submerge it under the water surface. The assembly was retrieved on August 08, 2001, at 10h00.

On August 1, 2001, at 13h30 the assembly was deployed in Lake St. Joseph (46°55'N, 71°40'W). The depth of the water at this location was 3 m. The assembly was attached to a rigid plastic rod, and was suspended 0.3 m from the sediment. Teflon[®] plaques were inserted into the sediment to mark the location of deployment. Buoys were not used at Lake St. Joseph due to the high motor boat traffic on the lake. The assembly was retrieved on August 08, 2001, at 16h30.

On August 2, 2001, at 14h00 the assembly was deployed at the McGill Biological Station (Green Bay) in Lake Memphremagog (44°5'-45°5'N, 72°0'-72°7'W). The depth of the water at this location was 3 m. The assembly was attached to a rigid plastic rod, and was suspended 0.3 m from the sediment. A plastic buoy, attached to a weighted monofilament nylon line, was submerged in proximity to the assembly and was used to mark its location. The assembly was retrieved on August 09, 2001, at 11h30.

Five Na-based DGT devices and three Ca-based DGT devices were used as process blanks and brought to each location. These devices were kept in plastic bags for the duration of the deployments. The bag was opened to the atmosphere upon retrieval of the Lake Tantaré assembly. The background concentrations of trace metals in the extracts were used to correct the concentration extracted from the deployed probes at each location.

Upon retrieval the peepers were removed from the assembly. The DGT devices were rinsed with copious volumes of deionized water (to stop metal diffusion) and placed into plastic bags. The DGT units were placed in the cooler and kept horizontal until they were dismantled, once back at the Ryerson University Trace Metal Clean Laboratory. The overlying filter and hydrogel layers were removed with plastic tweezers and discarded. The resin gels were carefully placed into 8-mL HDPE bottles and spiked with HNO₃ (Seastar; Sidney, BC) to

give a final volume of 5 mL (volume of eluent and resin hydrogel) of 2 M HNO₃. The concentration of metals in the eluent (C_e) was analyzed using GFAAS.

5.2.4 Calculation of DGT-labile “Organic” and “Inorganic” Concentrations

The concentration of DGT-labile “organic” and labile “inorganic” metal species in Lakes Tantaré, St. Joseph and Memphremagog were calculated using DGT devices with “open” and “tight” hydrogels by plotting $M_{DGT}/[(At/\Delta g)D_{inorg}]$ versus D_{org}/D_{inorg} from equation 10:

$$M_{DGT}/[(At/\Delta g)D_{inorg}] = C_{inorg} + (D_{org}/D_{inorg})C_{org} \quad (10)$$

where the mass of metals accumulated on the resin gel (M_{DGT}) of DGT devices fitted with the 0.10-cm “open” and “tight” hydrogels were corrected for their specific elution factor (Table 10) using equation 2. The diffusion coefficients of metals (D_{inorg}) and organic matter (D_{org}) in the “open” and “tight” hydrogels were the mean apparent tracer diffusion coefficients measured using the diaphragm diffusion cells (Table 3 and Table 6), with the exception of Cd in Lake St. Joseph, which was the interpolated value (Table 3). The slope and the y-intercepts provided estimates of the “organic” and “inorganic” species respectively.

Estimates of the concentration of DGT-labile “inorganic” metal species in Lakes Tantaré, St. Joseph and Memphremagog were calculated with the Na-based DGT devices and Ca-based DGT devices fitted with 0.10-cm “tight” hydrogels” using equation 7:

$$M_{inorg} = (D_{inorg}C_{inorg}At)/\Delta g \quad (7)$$

The diffusion coefficients of metals (D_{inorg}) in the “tight” hydrogels were the mean apparent tracer diffusion coefficients measured using the diaphragm diffusion cell, with the exception of Cd in Lake St. Joseph, which was the interpolated value (Table 3).

5.2.5 Water Quality Parameters

At the time of retrieval, 2-8 mL lake water samples were pipetted from the peepers into 8-mL HDPE bottles for total dissolved metals analysis. The bottles were previously spiked with 80 μ L of 2 M HNO_3 for preservation. At each location, total dissolved metal process blanks were prepared by pipetting 8 mL of deionized water into an acid-clean 8 mL bottle spiked with 80 μ L of 2 M HNO_3 . The sample bottles were stored in a cooler and placed in a freezer upon returning to Ryerson University. Total dissolved metal concentrations were analyzed using GFAAS.

In addition to total dissolved metals, samples were taken for DOC measurements from the peepers. For DOC measurements, 2-4 mL samples were pipetted into dark amber bottles acidified with 35 μ L of 0.1 N HCl. A DOC blank was prepared by pipetting 4 mL of UV treated deionized water (stored in dark amber bottle) into an amber bottle at each lake. DOC concentrations were analyzed at the INRS-ETE using a carbon analyzer (Shimadzu TOC-5000A).

Water quality parameters such as temperature, and pH were measured *in situ* at the depth of deployment and time of retrieval. The temperature was measured using a dissolved oxygen meter (YSI, model 50). The pH was measured using a portable pH meter (Hanna Instruments).

5.3. RESULTS

5.3.1 Water Quality Parameters

Total dissolved Mn determined for Lake Tantaré (116 nM) was approximately 4-fold and 6-fold greater than the total dissolved Mn concentrations in Lakes St. Joseph and Memphremagog, respectively (Table 13). The total dissolved concentration of Cd was 82

detectable in Lake Tantaré (0.20 nM), but was below analytical detection limits in Lakes St. Joseph and Memphremagog. Concentrations of total dissolved Pb were below the analytical detection limits in all three lakes (Table 13).

Concentrations of dissolved organic carbon (DOC) were relatively low for all three lakes (< 3.5 mg /L) (Table 13). The acidity of each lake differed; Lake Tantaré was acidic, Lake St. Joseph was circum-neutral and Lake Memphremagog was alkaline (Table 13).

Table 13. *Water quality parameters measured in Lakes Tantaré, St. Joseph, and Memphremagog (n.d. = not detectable).*

Lake	Total dissolved metal (<0.2 µm; nM)			DOC (mg /L)	Temp. (°C)	pH
	Mn	Cd	Pb			
Tantaré	116 ± 22	0.20 ± 0.04	n.d.	2.36 ± 0.02	23.0	4.65
St. Joseph	28 ± 4	n.d.	n.d.	2.99 ± 0.02	23.8	6.83
Memphremagog	18 ± 3	n.d.	n.d.	3.43 ± 0.03	25.0	8.21

5.3.2 Determination of Diffusive Boundary Layer (dbl) and Diffusive Layer

The dbl for each lake was determined by plotting 1/mass of Mn (mol⁻¹) fixed by resin hydrogel versus the sum of the hydrogel and filter thicknesses (Fig. 6).

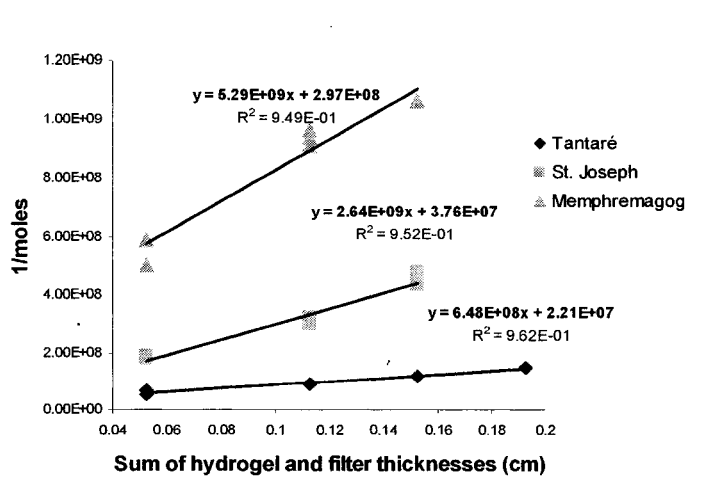


Figure 6. *Graphical determination of the diffusive boundary layers (dbl) for Lakes Tantaré, St. Joseph and Memphremagog.*

The negative value of the x-intercept of the equation of a best fit line estimates the mean dbf value for the duration of deployment. The calculated dbf value for Lake Memphremagog was approximately 4-fold greater than the dbf determined for Lake St. Joseph and approximately 1.6 times greater than the dbf determined for Lake Tantaré (Table 14). By summing the thicknesses of the mean dbf, hydrogel (0.10 cm) and filter (0.0125 cm) a diffusive layer thickness (Δg) was estimated for each lake (Table 14).

Table 14. *Determination of the mean diffusive boundary layer (dbf) and diffusive layer (Δg) thickness (cm) for Lakes Tantaré, St. Joseph, and Memphremagog.*

Lake	dbf (cm)	Δg (cm)
Tantaré	0.0341 ± 0.0132	0.1466
St. Joseph	0.0142 ± 0.1159	0.1267
Memphremagog	0.0561 ± 0.1280	0.1686

5.3.3 *In Situ* Measurements of Labile “Organic” and “Inorganic” Metals in Lakes Tantaré, St. Joseph, and Memphremagog

5.3.3.1 Manganese

Slopes of $M_{DGT}/[(At/\Delta g)D_{Mn}]$ versus D_{org}/D_{Mn} were negative for all three of the lakes tested, thereby estimating a negative concentration of DGT-labile “organic” Mn in these lakes (Figs. 7-9, Table 15). Alternatively, the concentrations of DGT-labile “inorganic” Mn in Lakes Tantaré, St. Joseph, and Memphremagog determined by the y-intercept of the graphs (Figs. 7-9) were considerably greater than the total dissolved metal concentration measured by *in situ* dialysis deployed in the same lakes (Tables 13 and 15). The concentration of DGT-labile “inorganic” Mn in Lake Tantaré was approximately 8-fold greater than the total dissolved metal concentrations measured by *in situ* dialysis. In Lakes St. Joseph and Memphremagog, the DGT-labile “inorganic” Mn concentrations were also found to be considerably greater than their total dissolved Mn concentrations measured by *in situ* dialysis (Tables 13 and 15).

To estimate the total DGT-labile concentration of Mn in these lakes requires summing the estimated DGT-labile “organic” and “inorganic” Mn concentrations. To determine if the slope of the relations were indeed negative (and therefore unphysical), the hypothesis that there was no significant difference between the magnitude of the y-axis values ($M_{DGT}/[(At/\Delta g)D_{Mn}]$) determined for the open and the tight hydrogels was tested using a Mann Whitney U test ($\alpha = 0.10$). If the values were not significantly different, then the slope of relation would equate to zero, inferring a negligible concentration of DGT-labile “organic” Mn. The results of the Mann Whitney U-Test indicated that indeed, the y-axis values ($M_{DGT}/[(At/\Delta g)D_{Mn}]$) determined for the open and the tight hydrogels were significantly different. The implications of this finding is that the total DGT-labile concentrations of Mn could not be computed using the graphical technique based on equation 10 due to the unphysical nature of the DGT-labile “organic” Mn concentration estimated from the slope of the relation.

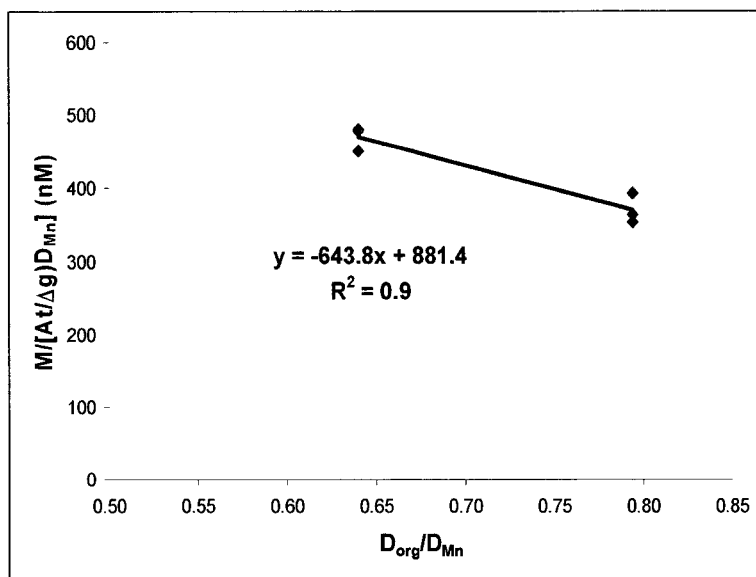


Figure 7. Determination of DGT-labile “organic” and “inorganically” bound Mn in Lake Tantaré using DGT devices fitted with both “open” and “tight” hydrogels.

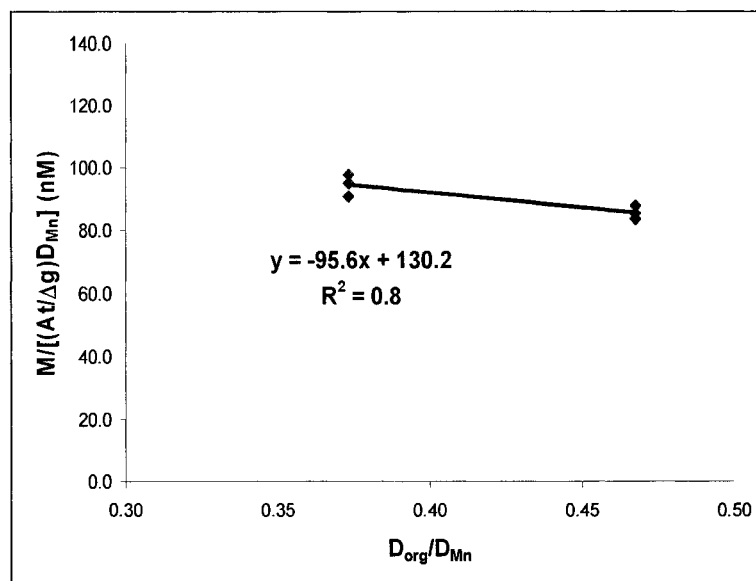


Figure 8. Determination of DGT-labile “organic” and “inorganically” bound Mn in Lake St. Joseph using DGT devices fitted with both “open” and “tight” hydrogels

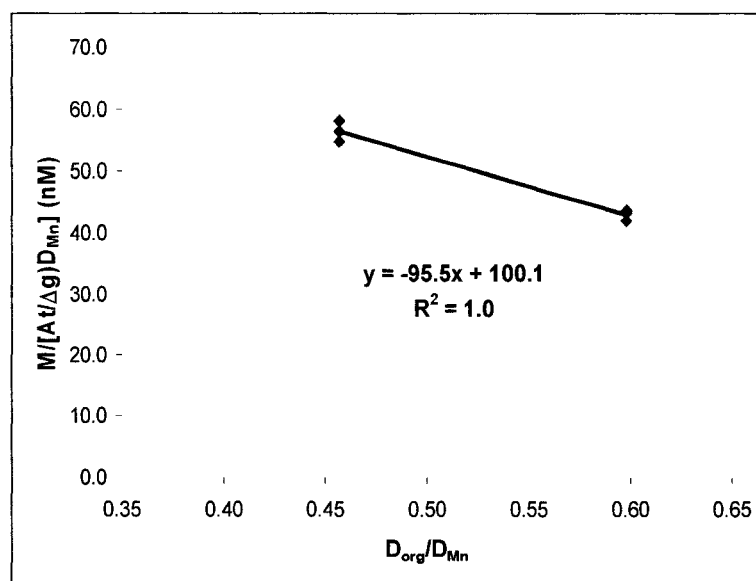


Figure 9. Determination of DGT-labile “organic” and “inorganically” bound Mn in Lake Memphremagog using DGT devices fitted with both “open” and “tight” hydrogels.

5.3.3.2 Cadmium

Plots of $M_{DGT}/[(At/\Delta g)D_{Cd}]$ versus D_{org}/D_{Cd} had positive slopes for Lake Tantaré and Lake St Joseph, indicating complexation of Cd with organics in these lakes (Table 15, Figs. 10-12). In Lake Tantaré, the fraction of DGT-labile “organic” Cd determined by the slope of Figure 10 was greater than the total dissolved metal concentration measured by *in situ* dialysis (Table 13). In Lake Memphremagog, the slope of $M_{DGT}/[(At/\Delta g)D_{Cd}]$ versus D_{org}/D_{Cd} was very shallow and slightly negative (-0.00 nM; Fig. 12), which resulted in a negative “organic” concentration (Table 15). To determine if the concentration of DGT-labile Cd in Lake Memphremagog was indeed negligible, the hypothesis that there was no significant difference between the magnitude of the y-axis values ($M_{DGT}/[(At/\Delta g)D_{Cd}]$) was tested using a Mann Whitney U-Test ($\alpha = 0.10$). The results of the test indicated that indeed the magnitude of the y-axis values were not significantly different, therefore the estimated DGT-labile “organic” concentration of Cd in Lake Memphremagog was negligible or 0 nM, allowing for the calculation of the total DGT-labile Cd in Lake Memphremagog.

The total DGT-labile concentration of Cd in Lake Tantaré overestimated the total dissolved concentration in the lake by 3-fold. In Lakes St. Joseph and Memphremagog, the concentrations of DGT-labile “organic” and “inorganic” Cd cannot be compared to the total dissolved Cd concentration in the lakes because the concentrations were below the detection limit of the analytical instrument.

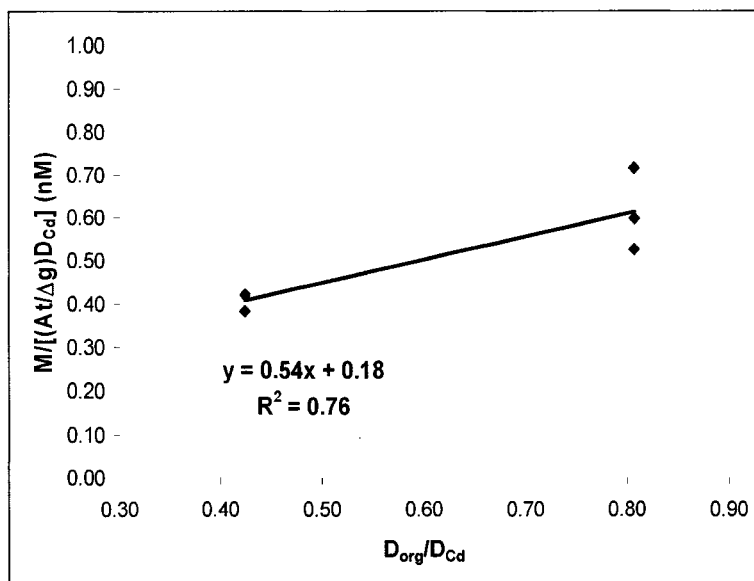


Figure 10. Determination of DGT-labile “organic” and “inorganically” bound Cd in Lake Tantaré using DGT devices fitted with both “open” and “tight” hydrogels.

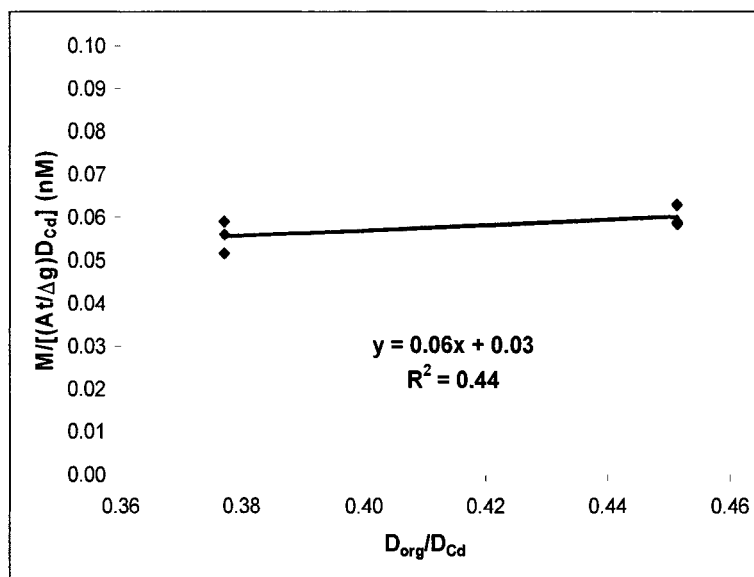


Figure 11. Determination of DGT-labile “organic” and “inorganically” bound Cd in Lake St. Joseph using DGT devices fitted with both “open” and “tight” hydrogels.

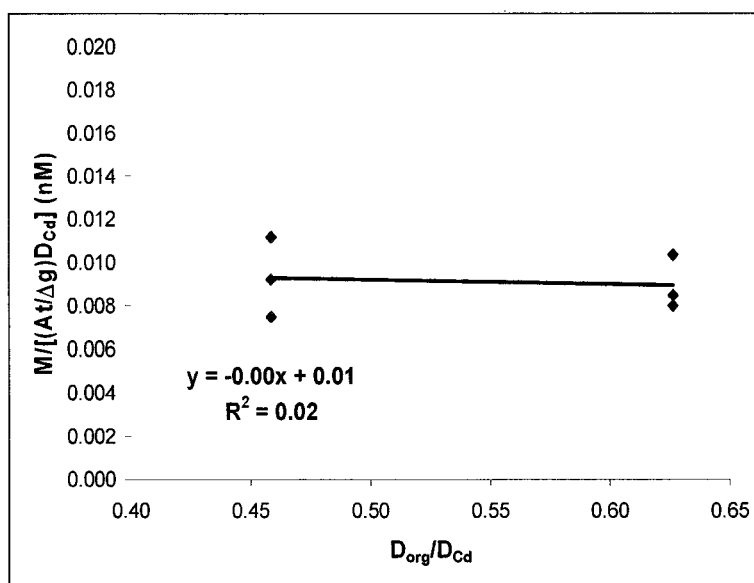


Figure 12. Determination of DGT-labile “organic” and “inorganically” bound Cd in Lake Memphremagog using DGT devices fitted with both “open” and “tight” hydrogels.

5.3.3.3 Lead

Similar to Mn, the slope of $M_{DGT}/[(At/\Delta g)D_{Pb}]$ versus D_{org}/D_{Pb} in Lake Tantaré was negative estimating a negative concentration of DGT-labile “organic” Mn (Fig. 13). Similar to Mn and Cd, a Mann Whitney U Test ($\alpha = 0.10$) was used to determine if the magnitude of the y-axis values ($M_{DGT}/[(At/\Delta g)D_{Pb}]$) were significantly different. Similar to Cd, the results of the test indicated that indeed the y-axis values were not significantly different, and therefore the DGT-labile “organic” concentration of Pb in Lake Tantaré was estimated to be negligible or 0 nM. Since the DGT-labile “organic” concentration of Pb in Lake Tantaré was estimated to be 0 nM, the total DGT-labile concentration of Pb in the lake could be estimated (0.34; nM Table 15). The concentration of Pb in the peeper was below the detection limit of the analytical instrument (Table 13), therefore the total DGT-labile concentration of Pb could not be compared to the total dissolved concentration of Pb in Lake Tantaré. In Lakes St. Joseph and Memphremagog, the concentrations of Pb in the eluent of the DGT devices and in the peepers

were below the detection limit of the analytical instrument, and therefore the DGT-labile fractions could not be computed (Table 15).

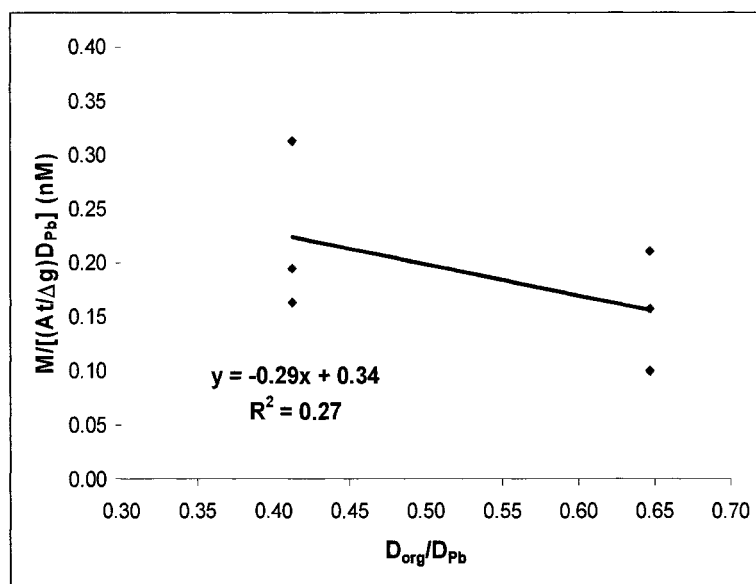


Figure 13. Determination of DGT-labile “organic” and “inorganically” bound Pb in Lake Tantaré using DGT devices fitted with both “open” and “tight” hydrogels.

Table 15. Mean DGT-labile “organic” and “inorganic” concentrations (nM, n=3) of Mn, Cd, and Pb in Lakes Tantaré, St. Joseph, and Memphremagog, using 0.10-cm “open” and “tight” hydrogels (n.d. = not detectable).

DGT-labile species	Tantaré			St. Joseph			Memphremagog		
	Mn	Cd	Pb	Mn	Cd	Pb	Mn	Cd	Pb
“Organic”	(-644 ± 98.06)	0.54 ± 0.15	(-0.29 ± 0.24)* 0	(-95.5 ± 24.87)	0.06 ± 0.03	n.d.	(-95.5 ± 7.65)	(-0.00 ± 0.01)* 0	n.d.
“Inorganic”	881 ± 70.71	0.18 ± 0.10	0.34 ± 0.13	130 ± 10.52	0.03 ± 0.01	n.d.	100 ± 4.07	0.01 ± 0.00	n.d.
Total	—	0.72 ± 0.18	0.34 ± 0.13	—	0.09 ± 0.04	n.d.	—	0.01 ± 0.01	n.d.

Notes: Values in parentheses are unphysical due to their negative nature

* Values were found to be not significantly different from 0 using a Mann Whitney U test ($\alpha = 0.10$)

(—) Total DGT-labile metal concentration could not be calculated due to unphysical nature of the DGT-labile “organic” metal concentration

5.3.4 *In Situ* Measurements of DGT-labile “Inorganic” Metal Species in Lakes Tantaré, St. Joseph, and Memphremagog

Although the concentration of labile “inorganic” Mn in the three lakes using the “tight” hydrogel devices were lower than those determined using both the “open” and “tight” hydrogels, the DGT-labile “inorganic” metal fraction was still overestimated (Table 16), as indicated by values greater than the measured total dissolved concentrations (Table 13).

The calculated concentration of labile “inorganic” Mn in Lake Tantaré (469 nM; Table 16) is approximately half that measured with the two hydrogel formulations (881 nM; Table 15), yet is still 4-times greater than the total dissolved Mn concentration measured in the lake (Table 13). Similarly, DGT-labile “inorganic” Mn in Lakes St. Joseph and Memphremagog were also lower than the concentration determined using the two hydrogel formulations, yet approximately 3-times greater than the total dissolved Mn concentrations measured in those lakes (Tables 13 and 16).

The concentration of DGT-labile “inorganic” Cd in Lake Tantaré (0.41 nM; Table 16) using the “tight” hydrogel devices was greater than the DGT-labile “inorganic” Cd determined using both the “open” and “tight” hydrogels (Table 15). The concentration of DGT-labile “inorganic” Cd in Lake Tantaré determined using the “tight” hydrogels (Table 16) was also greater than the measured total dissolved Cd concentration. Similarly for Lake St. Joseph, the DGT-labile “inorganic” concentration determined using the “tight” hydrogels (Table 16) was greater than the concentration determined using the two different hydrogel formulations (Table 15).

The concentration of DGT-labile “inorganic” Cd in Lake Memphremagog was calculated to be 0.01 nM using both techniques (Tables 15 and 16). Because the total dissolved

Cd concentration in Lakes St. Joseph and Memphremagog are below the detection limits of the analytical instrument, a comparison with the DGT-labile “inorganic” Cd could not be made.

The concentration of DGT-labile “inorganic” Pb in Lake Tantaré determined using the “tight” hydrogels was slightly lower (Table 16) than the concentration determined using both the “open” and “tight” hydrogels (Table 15). Because the total dissolved Pb in Lake Tantaré was below the detection limits of the analytical instrument, a comparison with the DGT-labile “inorganic” Pb could not be made.

Table 16. Mean concentration (nM, n=3) of DGT-labile “inorganic” Mn, Cd and Pb in Lakes Tantaré, St. Joseph, and Memphremagog using Na-based DGT devices and Ca-based DGT devices fitted with 0.10-cm “tight” hydrogels (n.d. = not detectable).

Resin gel	Metal	Lake		
		Tantaré	St. Joseph	Memphremagog
Na	Mn	469 ± 17*	94.4 ± 3.5§	56.5 ± 1.7
	Cd	0.41 ± 0.00	0.05 ± 0.00¶	0.01 ± 0.00
	Pb	0.22 ± 0.08	n.d.	n.d.
Ca	Mn	407 ± 33*	70.0 ± 9.8§	57.4 ± 17.2
	Cd	0.47 ± 0.05	0.08 ± 0.01¶	0.01 ± 0.00
	Pb	0.28 ± 0.11	n.d.	n.d.

Notes: * Values are significantly different, Mann Whitney U test ($\alpha = 0.10$)

§ Values are significantly different, Mann Whitney U test ($\alpha = 0.10$)

¶ Values are significantly different, Mann Whitney U test ($\alpha = 0.10$)

5.3.5 Comparison of Na-based and Ca-based DGT devices

Similar to the Na-based DGT devices, the Ca-based DGT devices overestimated the DGT-labile “inorganic” concentration of metals (Table 16), as indicated by values greater than the measured total dissolved concentrations. In Lake Tantaré, the DGT-labile “inorganic” concentrations of Mn and Cd measured by the Ca-based DGT devices were greater than the total dissolved concentration (4-fold and 2-fold respectively; Table 16). The concentrations of DGT-labile “inorganic” Pb in Lake Tantaré, and Cd in Lakes St. Joseph and Memphremagog measured by the Ca-based DGT devices could not be compared to the total dissolved

concentrations, because the total dissolved concentrations were below the detection limits of the analytical instrument.

Although the calculated concentrations of DGT-labile “inorganic” Mn measured by the Ca-based DGT devices were greater than the concentration of total dissolved Mn, in Lakes Tantaré and St. Joseph they were less than those measured by the Na-based DGT devices (Table 16). In the same lakes the concentrations of DGT-labile “inorganic” Cd and Pb measured by the Ca-based DGT were slightly greater than that measured by the Na-based DGT. The concentration of Mn and Cd measured by the Ca-based and Na-based DGT devices in Lake Memphremagog were similar.

To determine if the concentrations of metals measured by the Ca-based DGT devices were indeed similar or different, the hypotheses that there was no significant difference between the concentrations of Mn, Cd and Pb measured by the Na-based and Ca-based DGT devices was tested using a Mann Whitney U test ($\alpha = 0.10$). In contrast to the hypothesis that the Ca-based DGT devices would provide a more reasonable estimate of the labile metals concentrations in the lake, the test indicated the concentrations of DGT-labile “inorganic” Pb in Lake Tantaré, and DGT-labile “inorganic” Cd in Lakes Tantaré, St. Joseph, and Memphremagog measured by the Ca-based DGT devices were found not to differ from those measured with the Na-based DGT devices. The concentration of DGT-labile “inorganic” Mn measured by the Ca-based DGT devices differed from those measured with the Na-based DGT device in Lakes Tantaré and St. Joseph, although they were statistically similar in Lake Memphremagog.

5.4 DISCUSSION

5.4.1 *In Situ* Measurements of Labile “Inorganic” and “Organic” Metals in Lakes Tantaré, St. Joseph, and Memphremagog

It was hypothesized that the calculated concentrations of the total DGT-labile metal using the “open” and the “tight” hydrogels would overestimate the concentrations of metal in Lakes Tantaré and St. Joseph. As hypothesized, the DGT devices fitted with both the “open” and the “tight” hydrogels overestimated the concentrations labile metal concentrations in Lake Tantaré and Lake St. Joseph depicted by DGT-labile “inorganic” concentrations greater than those measured by *in situ* dialysis. Although the peepers were fitted with a 0.20- μm filter and the DGT devices contained a 0.45- μm filter, theoretically the DGT devices should only measure a fraction of the metals measured by *in situ* dialysis, due to the small pore size of the hydrogel (typically 2-5 nm; Davison and Zhang, 1994).

Interestingly, in all three lakes the concentration determined for the DGT-labile “inorganic” Mn was greater than the measured total dissolved Mn. Similar to the total DGT-labile concentration, the concentration of DGT-labile “inorganic” Mn should also be less than the concentration measured by *in situ* dialysis due to the smaller pore size of the hydrogel in the DGT device. In addition, in all three lakes the value determined for the DGT-labile “organic” concentration of Mn was negative. Since it is theoretically impossible to have a negative concentration of metals, this may indicate that the concentrations of DGT-labile “organic” Mn in these lakes are negligible. In general this is a reasonable assumption since Mn usually exists in an “inorganic” form and is not readily complexed by organics (Sunda, 1984). Yet statistical analysis using a Mann Whitney U test revealed that the slopes of the relations were indeed negative. Therefore, since it is physically impossible to have a negative concentration, the DGT technique of using hydrogels with two different formulations was

unable to provide reasonable estimates (for example 0 nM) of labile “organic” Mn concentrations in these lakes; a fundamental flaw in the DGT technique, as currently used.

Unlike Mn, the concentrations of DGT-labile “organic” Cd in Lakes Tantaré and St. Joseph estimated by the DGT technique are expected, because complexation of Cd in surface waters is common (Wells *et al.*, 1998). Although the concentration of DGT-labile “organic” Cd in Lake Memphremagog was estimated to be negative, the concentration was found to be negligible using a Mann Whitney U Test. Since metal complexes with organic (and inorganic) ligands tend to dissociate as pH decreases (Campbell and Stokes, 1985) it is interesting that the estimated concentration of DGT-labile “organic” Cd estimated for Lakes Tantaré and St. Joseph were greater than DGT-labile “organic” Cd estimated for Lake Memphremagog.

The negligible concentration of “organic” Pb in Lake Tantaré as estimated by the DGT technique and confirmed using the Mann Whitney U test may also be questionable. Since Pb is commonly found complexed by organic matter (Capodaglio *et al.*, 1990) and to a greater extent than Cd (Wells *et al.*, 1998), it would be assumed that an organic fraction would be present in Lake Tantaré. As with Cd, the speciation of Pb is sensitive to changes in pH (Campbell and Stokes, 1985), therefore, only a small fraction of organically complexed Pb may be expected in the acidic waters of Lake Tantaré.

In addition to the inability to provide reasonable estimates metal species, what is also surprising are the concentrations calculated using the DGT technique. The concentrations of DGT-labile “inorganic” Mn in Lakes Tantaré, St. Joseph and Memphremagog and the DGT-labile “organic” concentration of Cd in Lake Tantaré were all considerably greater than their measured total dissolved concentrations.

Comparisons of total DGT-labile Cd in Lakes St. Joseph and Memphremagog and Pb in Lake Tantaré with the total dissolved concentration is not possible. Yet the ability of the DGT-technique to measure concentration of these metals in lakes where the levels were too low for analysis by GFAAS is one of the advantages of the DGT technique that led to its rapid application to freshwater environments before being fully tested.

The ability to estimate negligible concentrations of DGT-labile “organic” Cd and Pb and not Mn using the DGT technique is interesting. This suggests that using hydrogels with two different formulations to estimate the labile “organic” and “inorganic” metal species may be specific to certain metals. Since Cd and Pb complex with organics in freshwaters then application of this technique to these metals is reasonable. Since Mn is not found to complex with organics in freshwaters, the application of the DGT technique to Mn is futile because it forces estimation of organic complexation.

The inadequacy of the DGT technique for measuring reasonable concentrations of DGT-labile “organic” and “inorganic” fractions of Mn, Cd, and Pb in the lakes may lie in the inability to accurately determine the diffusion coefficients of all inorganic and organic species present in the lakes. The empirically determined diffusion coefficients of the metal ions and natural organic matter using the diaphragm diffusion cell are considered to represent the diffusion of all of the forms of the metal (free, metal-inorganic complexes and metal-organic complexes) diffusing into the DGT device.

In lakes, the DGT technique will measure the “dissolved” fractions of metals (after passage through the 0.45- μm filter). These may include the free metal ion, metals complexed with simple inorganics (e.g. Cl^- , NO_3^- , OH^- , etc.), simple small metal-organic complexes (e.g. amino-acids, hydroxy-acids, etc) and complexes with large macromolecular ligands

(polysaccharides and humic substances) (Buffle, 1988). Diffusion coefficients of UV-absorbing organic matter (phenolic and benzene carboxylic compounds present in humic substances) are considered to represent the diffusion of all organic-metal fractions present in the lakewater. However, the diffusion coefficients of the smaller organic-metal molecules are not considered in the determination of “organic” and “inorganic” concentrations. The diffusion coefficients of these small organic-metal molecules (the amino acids and hydroxy-acids) will have much faster diffusion coefficients than the larger humic substances (because their diffusion will be less restricted in the hydrogel), and they will contribute to the mass of metal fixed by the resin gel in the DGT device. This phenomenon may be especially important in the “tight” hydrogels, where much of the “organic” fraction would be from the smaller organic-metal complexes; “tight” hydrogels may effectively exclude the large humic substances due to the decrease in hydrogel porosity. This variability in the diffusion coefficients of organic matter will incorrectly fractionate the “organic” and “inorganic” species. Organic-metal complexes with diffusion coefficients similar or close to that of the free metal ion or metal-inorganic complexes will be considered as “inorganic”, thereby underestimating the organic concentration and overestimating the inorganic concentration present in the lakewater. This may explain the overestimation of DGT-labile “inorganic” concentrations of Mn and Pb in Lake Tantaré, and Mn in Lakes St. Joseph and Memphremagog, since the DGT-labile “inorganic” concentration takes into account both the organic and inorganic metal species present in the lakes.

5.4.1.2 Reconciliation with Previous Studies

Zhang and Davison (2000) deployed replicate DGT devices with three different hydrogel porosities in an English stream; Greenhole Beck (pH 7.5 DOC 14.6 mg/L), for a

period of 35 hours. They assumed that the organic concentration in the river was dominated by fulvic acids, and, therefore, measured the diffusion coefficients of fulvic acid and the free metal ion in the three different hydrogels to calculate the DGT-labile “organic” and “inorganic” concentrations in the river. By plotting $M_{DGT}/[(At/\Delta g)D_{Cu}]$ versus D_{FA}/D_{Cu} , the DGT-labile “inorganic” concentration of Cu was determined to be 39% (11.8 nM) of the total DGT-labile concentration (30 nM) or, approximately 35% of the total “dissolved” metal concentration in the river (Zhang and Davison, 2000).

In a metal speciation study of similar rivers, Gardner *et al.* (2000) determined the chemical speciation of Cu in 15 English rivers ($pH\ 7.7 \pm 0.2$) using cathodic stripping voltammetry (CSV). Although they do not report the mean inorganic copper concentration of these rivers, it can be calculated to be approximately $3\% \pm 2\%$ of the measured total “dissolved” concentration from their results. In addition, they also found that humic substances (such as fulvic acids) were not largely responsible for the Cu complexation in these rivers. Rather complexation of Cu by other potential ligands such as amines, proteins, amino acids and carboxylic acids were found to be important (Gardner *et al.*, 2000).

The study conducted by Gardner *et al.* (2000) implies that the DGT technique overestimated the inorganic concentration of metals present in Greenhole Beck. In addition, using the diffusion coefficients of humic substances (rather than amines, proteins, carboxylic acids and amino acids) to represent the diffusion coefficient of organic-metal complexes, was not a valid method.

5.4.2 *In Situ* Measurements of DGT-labile “Inorganic” Metal Species in Lakes Tantaré, St. Joseph, and Memphremagog

5.4.2.1 Comparison of DGT-labile “Inorganic” Metal Species Determined using DGT Devices Fitted with both “open” and “tight” Hydrogels and DGT Devices Fitted with Only “tight” Hydrogels

It was hypothesized that the concentrations of DGT-labile “inorganic” metals measured by the DGT devices fitted with the “tight” hydrogels would not provide a reasonable measurement of DGT-labile “inorganic” concentration of metal species present in Lakes Tantaré and St. Joseph. As hypothesized, DGT devices fitted with only the “tight” hydrogels overestimated the “inorganic” concentrations of metals in Lakes Tantaré and St. Joseph, and in Lake Memphremagog. The concentration of DGT-labile “inorganic” Mn determined by the DGT devices fitted with the “tight” hydrogels was less than the concentration of DGT-labile “inorganic” Mn determined using the two hydrogel porosities. Yet, the concentrations of DGT-labile “inorganic” Cd and Pb calculated using the “tight” hydrogels were greater than the concentrations determined using the two hydrogel porosities. The calculated DGT-labile “inorganic” concentrations of Mn and Cd were greater than the total dissolved metal concentration measured in the lakes by the peepers. This indicated that the calculation of DGT-labile “inorganic” Mn and Cd using the “tight” hydrogels did not provide a reasonable estimate of the labile “inorganic” concentration of metals in the lakes as hypothesized.

The overestimation of Mn and Cd in Lake Tantaré and Mn in Lake St. Joseph is not surprising according to the hypothesis of Alfaro De la Torre *et al.* (2000). Alfaro De la Torre *et al.* (2000) hypothesized that in lakes with low cation concentrations, the overestimation of metal concentrations by the DGT device may be due to an increase in the diffusion coefficients of metal ions entering the DGT device due to the flux of Na from the resin gel. If correct, it is

possible that the diffusion cell may not accurately depict diffusion coefficients in the DGT devices in the lakes.

In general, the flux of metal ions is influenced by the concentration and concentration gradients of all other major ions in solution, in addition to being influenced by its own concentration gradient (Tessier *et al.*, 1994). Since the DGT devices measure a metal flux, the diffusion coefficients of metals entering DGT devices are influenced by the concentrations, concentration gradients, and diffusion coefficients of all the major cations including the Na^+ ions in the resin gel (Alfaro De-la Torre *et al.*, 2000). As Alfaro De-la Torre *et al.* (2000) hypothesized that in lakes with low cation concentrations, such as Lakes Tantaré and St. Joseph, the large negative concentration gradient of Na ions across the diffusive layer increases the diffusion coefficients of metal ions into the DGT device. In the diaphragm diffusion cell, the two compartments are filled with the same solution and separated by a hydrogel. Since the resin gel is absent, the negative concentration gradient formed from the diffusion of Na^+ ions is not present. The electrical component of Na on the diffusion coefficient of the metal ion being measured (Mn, Cd or Pb) in the hydrogel is not taken into consideration when calculating the diffusion coefficients for Lake Tantaré and Lake St. Joseph. Since the large negative concentration gradient of Na, has been hypothesized to increase the diffusion coefficients of the metal ions entering the hydrogel, the tracer diffusion coefficients determined would therefore underestimate the diffusion coefficients of these metal ions *in situ*. The underestimation of diffusion coefficients would result in an overestimation of bulk solution concentrations of metal ions, or rather the concentrations of metals measured in the lakes by DGT devices, as seen with Mn, and Cd in Lake Tantaré and Lake St. Joseph.

Conversely, the overestimation of metals may also be due to the measurement of metal-organic complexes by DGT technique not measured by *in situ* dialysis. As previously described, the DGT technique measures a metal flux, therefore metal ions are continuously diffusing into the DGT device, whereas *in situ* dialysis measures a total dissolved concentration of metals. When deployed into aquatic environments, a period of equilibration occurs in which metal ions diffuse into the compartments of the *in situ* dialysis samplers. After approximately two days the concentration of metals in the compartments of the samplers are at equilibrium with the metal concentration in the external medium. Theoretically, the concentration of metals measured by the DGT technique should be less than the total dissolved metal concentration measured by the peepers because the pore size of the hydrogel (approximately 2-5 nm) is considerably smaller than the filter membrane of the peepers (0.20- μm). Yet, Twiss and Moffett (2002) have demonstrated that strong metal-organic complexes (e.g. CuNTA) are in fact DGT-labile. Metal-organic complexes that are unable to pass through the filter membrane of the peepers ($> 0.20 \mu\text{m}$) but are small enough to pass through the filter of the DGT device ($< 0.45 \mu\text{m}$) may become labile within the measurement time and become a source of metal in the DGT technique. For long deployments (e.g. 1 week), these metal-organic complexes will accumulate at the filter-hydrogel interface and present a significant source of metals to the DGT technique. They will become labile within the measurement time, because the resin gel induces lability, and will diffuse through the hydrogel and become fixed by the resin gel. This may result in an apparent overestimation of labile metal concentrations estimated by the DGT technique when compared with total dissolved metal concentrations measured to the same extent by *in situ* dialysis. In freshwater environments where metal-organic complexes may play a significant role in metal speciation, the disparity in values

between the two techniques may demonstrate that the DGT technique does not behave ideal when deployed for prolonged periods.

The overestimation of Mn concentration in Lake Memphremagog by the DGT technique may be due to the dissociation of inorganic metal-ligand complexes to the free metal ion in the vicinity of the DGT device. As previously mentioned, in the peepers, after a short period of time (2 days; Davison *et al.*, 2000) the concentration of the free metal ion inside a cell are at equilibrium with the concentration of the free metal ion outside of the cell.

Alternatively, the DGT device acts as a sink, constantly removing the free metal ions from the external solution. Over time, the concentration of free metal ions in the vicinity of the DGT device will become depleted. Metal-ligand complexes (e.g. inorganic Mn-colloid) not measured by *in situ* dialysis will dissociate in an attempt to re-establish equilibrium with the surrounding waters. These free metal ions will diffuse into the DGT device and become measured by the resin gel. Zhang *et al.* (1998b) have reported that when DGT devices are deployed in soils they can induce lability of the metal ions in the soil. When the metal ions are removed from solution by the DGT device, this will induce a flux of metal ions from the soil to resupply the solution, and the concentration of the metal ions in solution will be effectively buffered to a constant value. This is identified when the value measured by the DGT device is greater than those measured using an independent analytical technique (Zhang *et al.*, 1998b).

5.4.2.2 Reconciliation with Previous Studies

These findings agree with those of a similar study conducted by Alfaro-De la Torre *et al.* (2000). In that study, replicate DGT devices and peepers were deployed into Lake Tantaré on two different occasions for one week. On both occasions, the concentrations of Cd and Ni measured by the DGT devices were greater than those measured by *in situ* dialysis in the lake.

Alfaro-De la Torre *et al.* (2000) attributed the overestimation of the values to the increase in diffusion coefficients of metals into the DGT device in lakes with a low concentration of cations ($\sum[\text{cations}] \leq 2 \times 10^{-4} \text{ M}$), yet Alfaro-De la Torre *et al.* did not consider the possible impact of metal-organic complexes on measurement made by the DGT devices.

Zhang and Davison (2000) hypothesized that DGT devices fitted with a hydrogel of small pore size can provide a reasonable estimate of the labile inorganic metal concentration in freshwater environments. The observed overestimation of DGT-labile “inorganic” concentrations by DGT devices with “tight” hydrogels suggests that DGT devices with hydrogels of small pore size in fact measure inorganic and organic-metal complexes, and do not provide a reasonable measurement of “inorganic” concentrations in freshwater environments as hypothesized.

5.4.3 Determination of DGT-labile “Inorganic” Mn, Cd and Pb Using Ca-based DGT Devices

5.4.3.1 Comparison of Na and Ca-based DGT Devices

In Lake Memphremagog, the resin gel formulation had no apparent effect on the estimated concentration of labile metal. The concentration of Mn in the lake was still overestimated by the Ca-based DGT device as well as with the Na-based DGT device. In contrast to the hypothesis that the Ca-based DGT devices would provide a more reasonable estimate of labile metal concentrations in the lakes, the effect of the resin gel formulation had no apparent effect on the measurement of DGT-labile Cd and Pb in lakes with a low cation concentration (Lakes Tantaré and St. Joseph). The concentration of DGT-labile “inorganic” Cd and Pb in Lakes Tantaré and St. Joseph either equaled (Cd and Pb in Lake Tantaré) or was only slightly greater (Cd in Lake St. Joseph) than the DGT-labile “inorganic” concentration measured by Na-based DGT devices. Therefore, under the low cation concentration conditions

of these lakes the Ca-based DGT device performed in a similar manner to the Na-based DGT device with these metals.

In comparison, the measured DGT-labile concentration of Mn by the Ca-based DGT devices in Lakes Tantaré and St. Joseph was slightly less than the concentration measured by the Na-based DGT devices as hypothesized, yet still greater than the measured total dissolved concentration measured by *in situ* dialysis. Since measurements of Cd and Pb were not impacted, this suggests that the concentration of Mn measured by the Ca-based DGT device was influenced by the formulation of the resin gel.

5.4.3.2 Reconciliation with Laboratory Studies

The behaviour of Mn, Cd and Pb in the Ca-based DGT device in this study differed from that observed in the laboratory study (Chapter 4). In the laboratory experiments, the mass of metals fixed by the Ca-based DGT devices were greater than those fixed by the Na-based DGT in the low cation concentration solution (2×10^{-5} M NaNO₃). This was attributed to an increase in the diffusion coefficients of the metal ions entering the Ca-based DGT devices, due to the complexation Ca²⁺ ions from the resin gel with functional groups present in the hydrogel. With the exception of Cd in Lake St. Joseph, these trends were not observed in this study. Rather, the concentrations of metals measured by the Ca-resin gel were equal to or less than the concentration of metals measured in the Na-based resin gel. The difference in results may be attributed to the duration of deployment and the selectivity of Chelex resin for metal ions.

In the laboratory experiment, the increased diffusivity of Mn, Cd and Pb in the low cation concentration solution was attributed to the greater efficiency of Ca compared to Na for binding with functional groups present in the hydrogel. In the Ca-based DGT device, less

functional groups would be available for complexation with the trace metals, allowing the metals ions to diffuse into the resin. In the field study, the DGT devices were deployed for a significantly longer period of time (7 days) which allowed for the saturation of the functional groups present in the hydrogel of both the Na-based and Ca-based DGT devices. This allowed the diffusion of the metal ions in hydrogel of the Na-based DGT device without being complexed by functional groups.

The difference in the behaviour of Mn, compared to Cd and Pb in the Ca-based DGT-devices may be attributed to the selectivity of the Chelex-100 resin for the metal ions. In accordance with the DGT theory, Mn, Cd and Pb will readily displace Na bound to Na-based resin because their selectivity for Chelex-100 are significantly greater than that of Na (Na: 10^{-7} , Pb: 3.88, Cd: 0.39, and Mn: 0.024 versus selectivity of Chelex-100 resin for Zn; BioRad, 2000). In the Ca-based DGT devices, the selectivity of the Chelex-100 resin for Cd and Pb are approximately between 30 and 300 times greater than that of Ca (0.013; BioRad, 2000). The selectivity of the Chelex-100 for Mn is only 2-fold the selectivity of Ca. Therefore, the Cd and Pb diffusing into the DGT devices will readily displace either Na^+ or Ca^{2+} ions bound to the Chelex-100 because their selectivity for Chelex-100 is significantly greater. Since the selectivity of Mn is close to that of Ca, but much greater than that of Na, its ability to displace Ca^{2+} ions bound to the Chelex-100 resin is significantly less than its ability to displace Na ions. Therefore, fewer Mn ions will be able to displace less Ca^{2+} ions from the Ca-based resin gel than Na^+ ions from the Na-based resin gel, leading to a lower concentration of Mn measured by the Ca-based DGT device.

With respect to the selectivity of different metals for the Chelex-100 resin, the results of this study suggest that the performance of Ca-based DGT device is more complex than

originally hypothesized. The findings also indicate that Ca-based DGT devices did not provide a reasonable measurement of DGT-labile “inorganic” metal concentrations in Lake Tantaré and Lake St. Joseph, and therefore do not provide an alternative to Na-based DGT devices in lakes with low cation concentrations as hypothesized. In addition, the inability to reconcile DGT-labile metal concentrations with the total dissolved metal concentrations using Ca-based DGT devices suggests that the measurement of metal-organic complexes by the technique may play a larger role in overestimating metal concentrations than previously hypothesized.

However, the ability of Mn to be influenced by the formulation of the resin gel devices does open up the possibility of charging the resin gel with more tightly bound cations. For example, if the resin gel is charged with a tightly held cation such as Zn, the ability of Pb to replace the cation from the Chelex-100 would be diminished. The selectivity of Chelex-100 for Pb is only approximately 4 times greater than its selectivity for Zn (Pb: 3.88 versus Zn: 1.00, as compared to the selectivity for Zn; BioRad, 2000). When deploying DGT devices equipped with a Zn charged resin gel, results similar to those determined for Mn in Lake Tantaré and St. Joseph may be observed for Pb. The affinity of Chelex-100 for Zn is approximately 3 times greater than the selectivity of Chelex-100 for Cd (Cd: 0.390 versus Zn: 1.00; BioRad, 2000). Therefore, in order for Cd to be measured, the resin gel would have to be charged with a cation less strongly held than Cd. This opens up the possibility of creating metal-specific DGT devices that must be charged with a specific cation in order to measure a certain metal. Although this was not the initial intent of the technique, if the accuracy of the technique is to be improved, it may provide a viable alternative.

5.4.4 Effect of the Diffusion Coefficients of Metals in the Diffusive Boundary Layer on DGT-labile Metal Calculations

These results assume that the diffusion coefficient of metal ions in the hydrogel, filter and dbL are equal to that determined in the hydrogel. Although this argument is not entirely valid, it does not represent one source of error associated with the DGT technique found in this study. Laboratory studies have determined that the diffusion coefficient of metal ions in Fye hydrogels with HVLP filters are not significantly different than those in Fye hydrogels without filters (Twiss and Stewart, unpubl.). Therefore, the assumption that the diffusion coefficient of metal ions in the HVLP filters is that determined for the hydrogel is valid in this study. In this study the diffusion coefficient of metal ions in the dbL is assumed to equal that of the diffusion coefficient in the hydrogel. Yet in actuality the diffusion of metal ions in the dbL is by molecular diffusion, and is therefore represented by the diffusion coefficient of metal ions in water. Since the diffusion coefficients of metal ions in the hydrogel are slower than those in the dbL, using these diffusion coefficients would therefore overestimate bulk solution metal concentrations. Therefore, equation 13 should be used to calculate the concentration of metals in the bulk solution:

$$C_b = (M_{DGT}/At)(\Delta g/^gD + \gamma/^fD + \delta/^wD) \quad (13)$$

where $^fD = ^gD$ for this study. The dbL determined for Lake Memphremagog was the largest (0.0561 cm; Table 14) of all three lakes and represented approximately 30% of the total diffusive layer. Using equation 13 the estimated concentration of DGT-labile Mn in Lake Memphremagog was 44.7 nM. Although this value is less than the DGT-labile metal concentrations 56.5 nM estimated for the Mn in Lake Memphremagog (Table 16), it still overestimates the labile metal concentration in the lake by approximately two-fold. This demonstrates that the overestimation of labile metal concentrations by the DGT-device was

independent of the equation used to calculate the labile metal concentrations, but rather a fundamental problem with the DGT technique applied in the current configuration.

5.4.5 Conclusions

The use of hydrogels of two different porosities did not provide reasonable estimates of DGT-labile “organic” and “inorganic” concentrations of Mn, Cd or Pb in lakes of varying cation concentrations and pH. The overestimation of the DGT-labile “inorganic” concentrations using this method may be attributed to the inability of the technique to accurately measure the diffusion coefficients of all organic species present, such as small-organic complexes that have similar diffusion coefficients as the free ion, or inorganic metal complexes. In addition the negative values ascribed to the DGT-labile “organic” concentrations of Mn are questionable and challenges to the validity of the technique for measuring metal speciation in freshwaters.

The DGT-labile “inorganic” concentrations of metals using DGT devices fitted with “tight” hydrogels did not provide a reasonable estimate of the labile inorganic metal concentrations in these same lakes. The overestimation of the inorganic concentration using this method may be due to either the measurement of metal-organic complexes not measured by *in situ* dialysis, or the inability to accurately measure diffusion coefficients in low cation concentrations using a diffusion cell.

Ca-based DGT devices did not provide a more reasonable measurement of metal concentrations present in Lake Tantaré and Lake St. Joseph when compared to the metal concentrations measured by *in situ* dialysis. This suggests that the performance of Ca-based DGT device is more complex in freshwaters than originally hypothesized, and therefore, does not provide an alternative to Na-based DGT devices in the lakes with low cation concentrations

for measuring Mn, Cd and Pb. However, the ability of the Ca-based DGT devices to measure concentrations of Mn less than those measured by the Na-based DGT devices does open up the possibility of charging the resin gel, with other more strongly bound, cations.

CHAPTER 6: EVALUATION OF THE DGT TECHNIQUE

This chapter identifies the important caveats associated with the DGT technique as they apply to freshwater environments. The methods used in this study, significant findings, and conclusions are reviewed. Based on the findings of this study, a critical evaluation of the ability of the technique to measure labile trace metal concentrations in freshwater environments is conducted.

6.1 CAVEATS ASSOCIATED WITH THE DGT TECHNIQUE

As discussed in previous chapters, many caveats associated with use of the DGT technique have been identified. Most of these caveats are centered on diffusion of metal ions and metal-complexing organic compounds in the diffusive layer. Twiss and Moffett (2002) found that strongly complexed organic-metal molecules were DGT-labile. Tessier and Goulet (unpubl.) determined that the diffusion of metal ions in the hydrogel and filter is dependent on solution conditions. Alfaro-De la Torre *et al.* (2000) found that the diffusion of trace metal ions in DGT devices are influenced by the co-diffusion of all other cations in solution.

6.2 REVIEW OF EXPERIMENTAL METHODS AND TECHNIQUES

In an attempt to measure DGT-labile metal concentrations, precaution was taken when designing the experimental methods used for this study considering the above-mentioned caveats. The following methods were used to control the recognized technical challenges associated with the technique:

1. Fye hydrogels which are relatively inert and have been found to be less reactive than AGE hydrogels in low ionic strength, high pH systems (Goulet and Tessier, unpubl.) were used for all experiments. Instead of using cellulose nitrate filters, HVLP filters (Millipore Corp; Bedford MA), were used as the protective membrane for all DGT deployments. The

diffusion coefficients of metals in these hydrogels have been found to equal that in the Fye hydrogels (Twiss and Stewart, unpubl.)

2. DGT devices were deployed *in situ* with hydrogels of two different formulations (“open” and “tight”) in an attempt to fractionate the DGT-labile “organic” and DGT-labile “inorganic” metal concentrations in the lakes (Zhang and Davison, 2000).
3. The diffusion coefficients of metal ions in the hydrogels were determined using solutions with a pH and cation concentration mimicking those of the lakes in which they were deployed. The diffusion coefficients of organic ligands in the hydrogels were determined using the natural organic matter in filtered lakewater samples.
4. As an alternative to the Na form of the resin gel, a Ca form of the resin gel was developed and also used in DGT devices when in freshwaters.

6.3 SUMMARY OF FINDINGS

The significant results of this study can be summarized as follows:

1. The diffusion coefficients of metals and organic matter in the hydrogels were influenced by solution conditions such as pH and cation concentration. This was recognized by metal diffusion coefficients greater than the tortuosity of the hydrogels in low cation concentration solutions, and the diffusion coefficients of organic matter in Lake Tantaré greater than those determined for Lake St. Joseph and Lake Memphremagog.
2. DGT devices equipped with Na-based resin gels and Ca-based resin gels were able to measure concentrations of Cd and Pb although the total dissolved concentration was less than the detection limit of the analytical technique (GFAAS).

3. DGT devices deployed with hydrogels of two different porosities were not able to provide reasonable estimates of DGT-labile “organic” and “inorganic” metal concentrations in the lakes studied.
4. The Na-based DGT devices equipped with “tight” hydrogels consistently overestimated DGT-labile metal concentrations (Mn and Cd) in all three lakes tested when compared with an independent measurement technique (*in situ* dialysis).
5. Ca-based DGT devices overestimated DGT-labile metal concentrations in the lakes when compared with an independent measurement technique (*in situ* dialysis). Yet concentrations of Mn measured by the Ca-based DGT devices were lower than those measured by the Na-based DGT devices in Lakes Tantaré and St. Joseph.

6.4 CONCLUSIONS

Based on the results of this study the following conclusions can be summarized:

1. The diffusion of both metals and organics are influenced by solution conditions. When deploying DGT devices in different lakes, the diffusion coefficient of metals and organics must be independently determined in the hydrogels for each lake.
2. The diffusion coefficients of metals in the DGT devices are more complex than originally hypothesized. The diaphragm diffusion cell may not accurately predict metal transport *in situ* because it does not consider the electrical effects of the resin gel on the diffusion coefficient of the metal ion of interest.
3. The Ca-based resin gel does not provide an alternative to the Na-based resin gel in freshwaters because it too overestimates labile metal concentrations. Charging the resin gel with more tightly held cations may provide an alternative to the Na-based resin gel.

4. Based on our current knowledge of the diffusion of metal-organic complexes in the DGT device, the technique is unable to provide reasonable measurements of “inorganic” and “organic” concentrations of metals.
5. The DGT technique does show promise as a method for measuring trace metal concentrations, because it is able to measure metal concentrations in lakewater that are undetectable using other measurement techniques (e.g. *in situ* dialysis).

6.5 EVALUATION OF TECHNIQUE

The ability of the DGT technique to measure concentrations of trace metals that may be otherwise not detectable renders it a favorable method for measuring trace metal concentrations in aquatic environments. In addition, the technique’s inherent simplicity, low cost, and robustness have led to its rapid application in freshwater environments before being validated through laboratory studies.

Initially the DGT technique emerged as an exciting new tool capable of measuring the bioavailable form of trace metals. Yet, the findings in this study have demonstrated that the technique in its current form cannot accurately measure labile metal concentrations in freshwater environments when compared with an independent measurement technique (*in situ* dialysis). These findings are significant, since it is equally important to determine in what environments the technique does not work, as well as in what environments it does work. The inability to reconcile DGT values with estimates of labile metal concentration in freshwaters, demonstrates our lack of knowledge of trace metal diffusion in the DGT devices when deployed in freshwater environments, and the requirement to conduct further laboratory testing. Of primary importance is undertaking experiments that would:

1. measure the diffusion coefficients of simple metal-organic complexes (e.g., amino-acids, hydroxy-acids and sugars) in hydrogels, and determine the importance of these complexes on the mass of metal measured by the technique;
 2. determine if large metal-organic complexes that are small enough to pass through the filter membrane of the DGT device, but too large for the filter membrane of the peepers, are capable of dissociating within the time frame of the experiment (7 days), and diffuse through the hydrogel and become fixed by the resin;
 3. ascertain if, by charging the resin gel with more tightly held metal cations (e.g., Zn), the technique can provide reasonable measurements of trace metals, such as Pb;
- and
4. establish the effect of the lack of resin gel in the diaphragm diffusion cell when measuring the diffusion coefficients of metal ions in hydrogels.

The implication of the requirement to conduct further laboratory testing is that the DGT technique should not be used in freshwater environments to provide accurate measurements of labile trace metal concentrations until the caveats of the technique have been resolved. In addition, extreme caution should be used when drawing conclusions regarding the concentrations of DGT-labile “organic” and “inorganic” metal species in any aquatic environment, since it has been found that deploying DGT devices equipped with hydrogels of different porosities overestimates the inorganic metal concentration relative to the organic metal concentration in aquatic environments.

APPENDIX

Table 17. *Calculation of the effective diffusion coefficients of Mn, Cd and Pb in $2 \times 10^{-5} M$ $NaNO_3$ using equation 11 (temperature corrected to 25°C).*

No	Ion	D_i (cm ² /sec)	sD_i (cm ² /sec)	z	Conc. in gel (mol/cm ³)	Δg cm	dC/dx (mol/cm ⁴)	sDeff (cm ² /sec)
1	Mn	6.88E-06	3.23E-06	2	5.00E-11	0.1158	4.32E-10	6.08E-06
2	Na(resin)	1.33E-05	6.25E-06	1	1.10E-07	-0.1158	-9.50E-07	
3	H	9.31E-05	4.38E-05	1	5.00E-09	0.1158	4.32E-08	
4	Cd	7.17E-06	3.37E-06	2	5.00E-11	0.1158	4.32E-10	6.33E-06
5	Pb	9.45E-06	4.44E-06	2	5.00E-11	0.1158	4.32E-10	8.35E-06
6	Na (bulk)	1.33E-05	6.25E-06	1	2.00E-08	0.1158	1.73E-07	
7	NO3-	1.15E-05	5.41E-06	-1	2.00E-08	0.1158	1.73E-07	

REFERENCES

- Alfaro-De la Torre, M.C., P.Y. Beaulieu, and A. Tessier. 2000. In situ measurement of trace metals in lakewater using dialysis and DGT techniques. *Anal. Chim. Acta*, **418**: 53-68.
- Anderson, M.A., F.M. Morel, and R.R.L. Guillard. 1978. Growth limitation of a coastal diatom by low zinc ion activity. *Nature*, **276**: 70.
- Apte, S., and G. Batley. 1995. Trace Metal Speciation of Labile Chemical Species in Natural Waters and Sediments: Non-Electrochemical Approaches. In *Metal Speciation and Bioavailability in Aquatic Systems*. Eds. A. Tessier and D.R. Turner. John Wiley & Sons, England. pp 259-299.
- Bates, S.S., A. Tessier, P.G.C. Campbell, and J. Buffle. 1982. Zinc adsorption and transport by *Chlamydomonas varibilis* and *Scenedesmus subspicatus* (Chlorophyceae) grown in semicontinuous culture. *J. Phycol.*, **18**: 521.
- Bio-Rad. 2000. Chelex 100 and Chelex 20 Chelating Ion Exchange Resin, Instruction Manual. Bio-Rad Laboratories. Hercules, CA.
- Borgmann, U., Norwood, W.P., and I.M. Babirad. 1990. Relationship between chronic toxicity and bioaccumulation of cadmium by *Hyalella azteca*. *Can. J. Fish. Aquat. Sci.* **48**:1055-1060.
- Buffle, J. 1988. Complexation Reactions in Aquatic Systems: an analytical approach. Ellis Horwood Limited, England. p. 2-20, 124.
- Buffle, J., and R.S. Altman. 1987. Interpretation of Metal Complexation by Heterogeneous Complexants. In: *Aquatic Surface Chemistry, Chemical Processes at the Particle-Water Interface*, Ed: W. Stumm. John Wiley and Sons, Toronto. pp. 352.
- Buffle, J., and G. Horvai. 2000. General Concepts. In: *In Situ Monitoring of Aquatic Systems*, Ed: J. Buffle and G. Horvai. John Wiley and Sons, N.Y. pp. 1-4.
- Campbell, P.G.C., and P.M. Stokes. 1985. Acidification and toxicity of metals to aquatic biota. *Can. J. Fish. Aquat. Sci.*, **42**: 2034-2049.
- Campbell, P.G.C. 1995. A Critique of the Free-Ion Activity Model. In: *Metal Speciation and Bioavailability in Aquatic Systems*. Eds. A. Tessier and D.R. Turner. John Wiley & Sons, England. pp 259-299.
- Campbell, P.G.C., M.R. Twiss, and K.J. Wilkinson. 1997. Accumulation of natural organic matter on the surfaces of living cells: implications for the interaction of toxic solutes with aquatic biota. *Can. J. Fish. Aquat. Sci.*, **54**:2543-2554.

- Capodaglio, G., K.H. Coale, and K.W. Bruland. 1990. Lead speciation in surface waters of the eastern north pacific. *Mar. Chem.*, **29**: 221-223.
- Carignan, R., F. Rapin, and A. Tessier. 1985. Sediment porewater sampling for metal analysis: A comparison of techniques. *Geochim. Cosmochim. Acta*, **49**: 2493-2497.
- Chang, L.Y., W. Davison, H. Zhang, and M. Kelly. 1998. Performance characteristics for the measurement of Cs and Sr by diffusive gradients in thin films (DGT). *Anal. Chim. Acta*, **368**: 243-253.
- Davison, W., and H. Zhang. 1994. In situ speciation measurements of trace components in natural waters using thin-film gels. *Nature*, **367**: 546-548.
- Davison, W., G. Fones, M. Harper, P. Teasdale, and H. Zhang. 2000. Dialysis, DET and DGT: In Situ Diffusional Techniques for Studying Water, Sediments and Soils. In: *In Situ Monitoring of Aquatic Systems*. Ed: J. Buffle and G. Horvai. John Wiley and Sons, N.Y. pp. 495-566.
- Davison, W. 1978. Defining the electroanalytically measured species in a natural water sample. *J. Electroanal. Chem.*, **87**: 395-404.
- Denny, S., J. Sherwood, and J. Leyden. 1999. *In situ* measurement of labile Cu, Cd and Mn in river waters using DGT. *Sci. Total Environ.*, **239**: 71-80.
- Dillon, P.J., and R. D. Evans. 1982. Whole-lake lead burdens in sediments of lakes in southern Ontario, Canada. *Hydrobiologia*. **91**:121-130
- Dunn, M.J. 1993. Gel Electrophoresis: Proteins. BIOS Scientific Publishers, Oxford, UK. pp. 13-16.
- Gardner, M., E. Dixon, and S. Comber. 2000. Copper complexation in English rivers. *Chem. Speciat. Bioavail.*, **12**:1-7.
- Gill, G., and K.W. Bruland. 1990. Mercury speciation in surface freshwater systems in California and other areas. *Environ. Sci. Technol.*, **24**: 1392-1400.
- Hames, B.D. 1981. Gel Electrophoresis of Proteins: A practical Approach. Eds. B.D. Hames and D. Rickwood. IRL Press Ltd. London, England. pp. 1-25.
- Hare, L., and A. Tessier. 1998. The aquatic insect *Chaoborus* as a biomonitor of trace metals in lakes. *Limnol. Oceanog.*, **43**(8): 1850-1859.
- Hering, J., and F. Morel. 1990. Kinetics of Trace Metal Implications for Metal Reactivity in Natural waters. In: *Aquatic Chemical Kinetics*, Ed: W. Stumm. John Wiley and Sons, Toronto. p.148.

- Hesslein, R. 1976. An in situ sampler for close interval pore water studies. *Limnol. Oceanogr.*, **21**: 912-914.
- Kaplan, L.A. 1994. A Field and laboratory procedure to collect, process and preserve freshwater samples for dissolved organic carbon analysis. *Limnol. Oceanogr.*, **39**(6): 1476-1481.
- Lead, J., K. Wilkinson, K. Starchev, S. Canonica, and J. Buffle. 2000. Determination of diffusion coefficients of humic substances by fluorescence correlation spectroscopy: role of solution conditions. *Environ. Sci. Technol.*, **34**: 1365-1369.
- Li, Y.H., and S. Gregory. 1974. Diffusion of ions in sea water and deep-sea sediments. *Geochim. Cosmochim. Acta*, **38**: 703-714.
- MacLean, R.S., U. Borgmann, and D.G. Dixon. 1996. Bioaccumulation kinetics and toxicity of lead in *Hyalella azteca* (Crustacea, Amphipoda). *Can. J. Fish. Aquat. Sci.*, **53**: 2212-2220.
- Morel, F. 1983. Principles of Aquatic Chemistry, Wiley-Interscience, New York. pp. 301.
- Millipore Corp. 1997. Operating and Maintenance Manual, Milli-Q®
- Mota, A.M., and M.M. Correia dos Santos. 1995. Trace Metal Speciation of Labile Chemical Species in Natural Waters: Electrochemical Methods in Metal Speciation and Bioavailability in Aquatic Systems. Eds. A. Tessier and D.R. Turner. John Wiley & Sons, England. pp. 205-258.
- Murdock, C., M. Kelly, L.Y. Chang, W. Davison, and H. Zhang. 2001. DGT as an in situ tool for measuring radiocesium in natural waters. *Environ. Sci. Technol.*, **35**: 4530-4535.
- Nriagu, J.O., H. Wong, G. Lawson, and P. Daniel. 1998. Saturation of ecosystems with toxic metals in Sudbury basin, Ontario, Canada. *Sci. Total Environ.*, **223**: 99-117.
- Nriagu, J.O., G. Lawson, H. K.T. Wong, and J. Azcue. 1993. A protocol for minimizing contamination in the analysis of trace metals in Great Lakes waters. *J. Great Lakes Res.*, **19**(1): 175-172
- Price, N., G. Harrison, J. Hering, R. Hudson, P. Nirel, B. Palenik, and F. Morel. 1989. Preparation and chemistry of the artificial algal medium aquil. *Biol. Oceanogr.*, **6**: 443-461.
- Sigg, L. 1994. Regulation of Trace Elements in Lakes: The Role of Sedimentation. In: Chemical and Biological Regulation of Aquatic Systems. Eds: J. Buffle and R. De Vitre. CRC Press, Boca Raton. pp. 177-178.
- Sunda, W.G. 1984. Measurement of manganese, zinc and cadmium complexation in seawater using Chelex ion exchange equilibria. *Mar. Chem.*, **14**: 365-378.

Tessier, A., and D.R. Turner. 1995. Preface In: Metal Speciation and Bioavailability in Aquatic Systems. Eds. A. Tessier and D.R. Turner. John Wiley & Sons, England. pp. xii-xv.

Tessier, A., R. Carignan, and N. Belzile. 1994a. Processes occurring at the sediment-water interface: Emphasis on trace elements. In: Chemical and Biological Regulation of Aquatic Systems. Eds. J. Buffle and R. De Vitre. CRC Press, Boca Raton. pp. 137-173.

Tessier, A., J. Buffle, and P.G. C. Campbell. 1994b. Uptake of Trace Metals by Aquatic Organisms. In: Chemical and Biological Regulation of Aquatic Systems. Eds. J. Buffle and R. De Vitre. CRC Press, Boca Raton. pp. 197-230.

Tipping, E. 1994. WHAM-a chemical equilibrium model and computer code for waters, sediments, and soils incorporating a discrete site/electrostatic model of ion-binding by humic substances. *Comput. Geosci.*, **20**(6): 973-1023.

Turner, D. 1995. Problems in Trace Metal Speciation Modeling. In Metal Speciation and Bioavailability in Aquatic Systems. Eds. A. Tessier and D.R. Turner. John Wiley & Sons, England. pp. 149-203.

Twiss, M., and J. Moffett. 2002. A comparison of copper speciation in coastal marine waters estimated using analytical voltammetry and diffusion gradient in thin film (DGT) techniques. *Environ. Sci. Technol.*, **36**: 1061-1068.

Wang, J. H., C. V. Robinson, and I.S. Edelman. 1953. Self-diffusion and structure of liquid water. III. Measurement of the self-diffusion of liquid water with H₂, H₃, and O₁₈ as tracers. *J. Amer. Chem. Soc.*, **75**: 466-470.

Wells, M., P. Kozelka, and K.W. Bruland. 1998. Complexation of "dissolved" Cu, Zn, Cd and Pb by soluble and colloidal organic matter in Narragansett Bay, RI. *Mar. Chem.*, **62**: 203-217.

White, M.L., and G.H. Dorion. 1961. Diffusion in a crosslinked acrylamide polymer gel. *J. Polymer Sci.*, **55**: 731-740.

Wilkinson, K., A. Joz-Roland, and J. Buffle. 1997. Different roles of pedogenic fulvic acids and aquagenic biopolymers on colloid aggregation and stability in freshwaters. *Limnol. Oceanogr.*, **42**(8): 1714-1724.

Xue, H., and L. Sigg. 1998. Cadmium speciation and complexation by natural organic ligands in fresh water. *Anal. Chim. Acta.*, **363**: 249-259.

Xue, H., and W. Sunda. 1997. Comparison of Cu²⁺ measurements in lake water determined by ligand exchange and cathodic stripping voltammetry and by ion-selective electrode (potentiometry). *Environ. Sci. Technol.*, **31**: 1902-1909.

Zhang, H., and W. Davison. 1995. Performance characteristics of diffusion gradients in thin films for the *in situ* measurement of trace metals in aqueous solution. *Anal. Chem.*, 67: 3391-3400.

Zhang, H., W. Davison, S. Miller, and W. Tych. 1995. *In situ* high resolution measurements of fluxes on Ni, Cu, Fe and Mn and concentrations of Zn and Cd in porewaters by DGT. *Geochim. Cosmochim. Acta*, 59: 4181-4192.

Zhang, H., W. Davison, R. Gadi, and T. Kobayashi. 1998a. *In situ* measurement of dissolved phosphorus in natural waters using DGT. *Anal. Chim. Acta.*, 380: 29-38.

Zhang, H., W. Davison, B. Knight, and S. McGrath. 1998b. *In situ* measurements of solution concentrations and fluxes of trace metals in soils using DGT. *Environ. Sci. Technol.*, 32: 704-710.

Zhang, H., and W. Davison. 1999. Diffusional characteristics of hydrogels used in DGT and DET techniques. *Anal. Chim. Acta.*, 398: 329-340.

Zhang, H., and W. Davison. 2000. Direct *in situ* measurements of labile inorganic and organically bound metal species in synthetic solutions and natural waters using diffusive gradients in thin films. *Anal. Chem.*, 72: 4447-4457.