DIFFUSIVE GRADIENTS IN THIN-FILMS FOR ENVIRONMENTAL MEASUREMENTS

The diffusive gradients in thin-films (DGT) technique is a means of measuring the concentration and speciation of elements in natural waters. Edited by one of the pioneers of the technique, this unique volume provides a complete and authoritative guide to the theory and applications of DGT.

The book includes explanations of the fundamental principles of DGT, accessible to readers with a modest background in chemistry, as well as more advanced chapters that provide a thorough treatment of the physical and chemical dynamics of this technique and evaluate how well it mimics the biological uptake process. Chapters on natural waters, soils and sediments illustrate the applications of DGT, and detailed instructions are included on how to use DGT in practice.

Combining the fundamentals of DGT with more advanced principles, this is an indispensable text for students, researchers and professional scientists interested in the chemistry of natural waters, soils and sediments.

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Preface

As scientists from a range of disciplines begin to use DGT, they inevitably ask, "How do I learn about it? What should I read?" Until now the answer has been a range of publications, as none alone have provided a comprehensive overview or the practical details essential to getting started. Hopefully this book will do just that. Hao Zhang and I first started to write such a book about seven years ago, but we soon put it on hold when we realized firstly that there seemed to be more questions than answers and secondly that the increasing breadth of the applications of DGT was stretching our expertise. So when Laura Sigg on behalf of Cambridge University Press approached us shortly after the 2013 DGT Conference to write this book we were initially reluctant, while recognizing the need. Eventually we realized that the answer to our problems might be an edited volume. We still wanted a "text book", so we designed the chapters accordingly and selected key authors who we knew would bring expertise and thoroughness to their allocated chapter topics. Hao chose to relinquish her editorial role due to her extensive commitments, but has contributed to valuable chapters. Sometimes it is wise to wait and this is certainly the case for this book. There have been many developments of the method and new applications in the past seven years. Most of the contents of three chapters, dealing with understanding the DGT measurement in the presence of dynamic complexes, appreciating its ability to mimic some types of biological uptake processes, and two-dimensional imagery of analytes in soils and sediments, have only emerged in the past few years. This book is certainly timely with respect to understanding the DGT measurement, but that does not mean that progress has plateaued. Far from it, as the capability for measuring an increasingly wider range of analytes is being matched by new, high-performance binding layers, I have little doubt that development of this truly versatile technique will continue at pace. Hopefully this book will still be useful in providing the foundations for the theory and practice of DGT.

I would personally like to thank the contributing authors. They have made good use of their specialist expertise while adhering well to the brief, to produce chapters that are authoritative and yet accessible to non-specialists. In its short history many people have shared in the development of DGT. I am especially grateful to my many collaborators and to those students, research staff and visitors who have spent time in the laboratory of Hao and I and shared their thoughts and contributions on DGT.

Symbols and Abbreviations

Units

C	coulombs
g	gram
L	litre
M	moles L^{-1}
s	second
d	day
V	volt
m	milli (10^{-3})
μ	micro (10^{-6})
n	nano (10^{-9})
p	pico (10^{-12})
f	femto (10^{-15})

Symbols		example unit
A	area of DGT sampling interface (used in DGT calculation)	cm^2
A_p	geometric area of the DGT device window	cm^2
A_E	effective area of the binding layer that accumulates analyte	cm^2
b	soil buffer power	
c	concentration of solute	nM, ng L^{-1}
c_e	concentration of analyte in the eluent	nM, ng L^{-1}
c_E	effective concentration in soil or sediment	nM, ng L^{-1}
c^{soln}, c^*	concentration of solute in the deployment or bulk solution	nM, ng L^{-1}
c^g	steady-state concentration at the outer surface of the diffusive gel	nM, ng L^{-1}
c^f	steady-state concentration at the outer surface of the filter	nM, ng L^{-1}
c^i	instantaneous concentration at DGT–medium interface	nM, ng L^{-1}
c^{ls}	concentration of labile analyte in the solid phase[1]	nM, ng L^{-1}
c^s	sorbed concentration	nM, ng L^{-1}
$c_{T,L}$	total concentration of all ligand species	nM, ng L^{-1}

Symbols		example unit
c_{lab}	concentration of all labile species[1]	nM, ng L^{-1}
c_{DGT}	concentration from DGT simple equation	nM, ng L^{-1}
c^{bio}	internal concentration in biota	nM, ng L^{-1}
c^{bio}_{min}	minimum internal concentration in biota	mg, kg^{-1}
c^{bio}_{tox}	toxic threshold concentration in biota	mg, kg^{-1}
c_{diff}	mean interfacial concentration for diffusional supply only	nM, ng L^{-1}
c^{gel}	concentration of analyte in gel	nM, ng L^{-1}
c^{dyn}_{max}	dynamic maximum concentration	nM, ng L^{-1}
c_M	free metal ion concentration in bulk solution	nM, ng L^{-1}
c_{M0}	free metal ion concentration at the root surface	nM, ng L^{-1}
D	diffusion coefficient of analyte	$cm^2\ s^{-1}$
D_i	diffusion coefficient of species i	$cm^2\ s^{-1}$
D^{mdl}	diffusion coefficient of analyte in material diffusion layer	$cm^2\ s^{-1}$
D^g	diffusion coefficient of analyte in the diffusive gel layer	$cm^2\ s^{-1}$
D^f	diffusion coefficient of analyte in the membrane filter	$cm^2\ s^{-1}$
D^w	diffusion coefficient of analyte in water (e.g. in DBL)	$cm^2\ s^{-1}$
D^s	diffusion coefficient in soil or sediment	$cm^2\ s^{-1}$
F	Faraday constant	C mol^{-1}
f_e	elution factor	
f_u	uptake factor	
g^p_{kin}	kinetic term in units of distance	cm
h	number of ligands	
i	interface	
I	ionic strength	mol L^{-1}
J	flux	fmoles $s^{-1}\ m^{-2}$
J_{diff}	area-based diffusive flux	fmoles $s^{-1}\ m^{-2}$
J_{free}	diffusion flux if only the free ion contributed	fmoles $s^{-1}\ m^{-2}$
J_{labile}	flux if all metal species are labile	fmoles $s^{-1}\ m^{-2}$
J_{max}	maximum flux (Michaelis–Menten)	fmoles $s^{-1}\ m^{-2}$
J_{tot}	diffusion flux if all metal behaves as the free ion	fmoles $s^{-1}\ m^{-2}$
J_{upt}	uptake flux	fmoles $s^{-1}\ m^{-2}$
K	stability constant	M^{-1}
K'	normalized concentration of complex ($= c^*_{ML}/c^*_M = K/c^*_L$)	
K_d	partition coefficient	$cm^3\ g^{-1}$

[1] There is a difficulty in using concentrations of labile species, because different species have different labilities, which will vary depending on the measurement used. However, sometimes it is convenient to represent a concentration of labile species. When this is done, the imprecise nature of such a symbol is recognised in the text.

Symbols		example unit
K_{dl}	labile partition coefficient	$cm^3\ g^{-1}$
K_i	binding constant for competing ion X_i	M^{-1}
K_m	Michaelis–Menten constant	$mol\ L^{-1}$
K_M	binding constant for metal	M^{-1}
K^{os}	outer sphere stability constant	M^{-1}
$K_{Xi\ BL}$	biotic ligand binding constant of ion X_i	M^{-1}
k_1	sorption rate constant	s^{-1}
k_{-1}	desorption rate constant	s^{-1}
k_a	association rate constant	$M^{-1}\ s^{-1}$
k_d	dissociation rate constant	s^{-1}
$k_{a,R}$	rate constant for association to resin	$M^{-1}\ s^{-1}$
$k_{d,R}$	rate constant for dissociation from resin	s^{-1}
k_L	association rate with surface ligand	$cm^3\ mol^{-1}\ s^{-1}$
k_{-w}	rate constant for removal of a water molecule	s^{-1}
L	ligand	
L_T	density of surface ligands	$mol\ cm^{-2}$
l	length, distance	cm
M	metal	
M	mass of analyte on the binding layer	pg
M_f	final mass	pg
M_i	initial mass	pg
M_p	mass of particles	g
M_{wt}	molecular mass	$g\ mol^{-1}$
m	disequilibrium parameter	cm
n	number of moles of analyte in the binding layer	pmol
P_c	particle concentration (weight in volume of soil/sediment)	$g\ cm^{-3}$
P_{diff}	diffusional permeability	$cm\ s^{-1}$
P_m	membrane permeability	$cm\ s^{-1}$
Q	concentration quotient	M^{-1}
Q_i	internal concentration	μM
$Q_{i(min)}$	minimum internal concentration	μM
$Q_{i(tox)}$	toxic threshold of internal concentration	μM
q_i	normalized concentration of species i (e.g. $q_{ML} = c_{ML}/c^*_{ML}$)	
R	resin	
R	correlation coefficient or gas constant	
R_c	c_{DGT}/c^{soln} in soils and sediments	
r_o	radius	cm
s	slope	
T	temperature	^oC
T^K	absolute temperature	^oK
t_c	response time to perturbation	s
t	time	s
t_e	equilibration time	s

Symbols		example unit
t_{ss}	time to achieve steady state	s
u_g	specific growth rate	s^{-1},d^{-1}
U	flow velocity	cm s^{-1}
V^{bl}	volume of binding layer	mL
V_e	volume of eluent	mL
V_s	volume of soil	cm^3
V_{MWHC}	soil maximum water holding capacity	% (*W*/*W*)
v_0	rate of water advection	cm d^{-1}
W	weight	g
$W_{1/2}$	width of peak at half height	cm
x	perpendicular distance from plastic base	cm
Xi	activity of ion i	M
X_i	ion i	
y	intercept	
z_C	valence of cations	
z_{SE}	valence of supporting electrolyte	
z_i	number of charge of species *i*	
α	root absorption power	cm s^{-1}
γ_i	activity coefficient of species *i*	
δ	geochemical delta value of isotope	
δ	general diffusion layer thickness	cm
δ^g	thickness of the diffusive gel layer	cm
δ^f	thickness of the membrane filter	cm
δ^{mdl}	thickness of material diffusion layer ($= \delta^g + \delta^f$)	cm
Δg	thickness of material diffusion layer ($= \delta^{mdl}$)	cm
δ^r	thickness of binding layer	cm
δ^{dbl}	thickness of the diffusive boundary layer	cm
ε	normalized complex diffusion coefficient (D_{ML}/D_M)	
η	viscosity of water	Pa s
θ	volumetric moisture content	
θ_T	tortuosity	
λ_M	metal penetration parameter	cm
λ_{ML}	complex penetration parameter	cm
μ	reaction layer thickness	cm
υ	kinematic viscosity	cm^2 s^{-1}
Π	Donnan partition factor	
ξ	lability degree	
ρ^g	charge density of gel	C cm^{-3}
ρ^b	soil bulk density	g cm^{-3}
ρ^s	density of solid phase material	g cm^{-3}
φ	porosity	
ψ	Donnan potential	V

Abbreviations

AAS	atomic absorption spectroscopy
APA	polyacrylamide gel cross-linked with an agarose derivative
APS	ammonium persulphate
AVS	acid volatile sulphur
BLM	biotic ligand model
CID	computer imaging densitometry
DBL	diffusive boundary layer
DET	diffusive equilibration in thin-films
DGT	diffusive gradients in thin-films
DOC	dissolved organic carbon
DOM	dissolved organic matter
$EC50_{free}$	50% effect concentration (free ion based)
$EC50_{free}{}^{*}$	50% effect (free) concentration in absence of competing ions
FIAM	free ion activity model
FIP	first ionisation potential
FA	fulvic acid
GF-AAS	graphite furnace atomic absorption spectroscopy
HA	humic acid
HPW	high purity water
HS	humic substances
HSI	hyperspectral imaging
IAP	ion activity product
IC	ion chromatography
ICP-MS	inductively coupled plasma mass spectrometry
LA	laser ablation
LOD	limit of detection
MDL	material diffusion layer (diffusive gel and membrane filter)
MUF	4-methylumbelliferyl
OM	organic matter
PIXE	proton induced x-ray emissions
SD	standard deviation
SEM	simultaneously extracted metals
SI	saturation index
SPR-IDA	suspended particulate reagent iminodiacetic acid
TEMED	tetramethylethylenediamine
TWA	time weighted average concentration
UPW	ultra pure water
UV	ultraviolet
WHAM	Windermere humic acid model