Diffusive Gradients in Thin Films (DGT) as a technique to predict nutrient availability to plants

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Abstract

The soils of Australia have extensive macro and micronutrient disorders varying greatly in their capacities to provide the chemical nutrients essential for plant growth. Assessment of nutrient availability in soils is important in order to maximise fertilizer efficiency and crop yields and to minimise environmental pollution associated with over fertilisation. Nutrient availability has proven difficult to assess due to the complexity of trace element soil chemistry and plant uptake mechanisms. The relatively new method, Diffusive Gradients in Thin Films (DGT), provides the potential to become an alternative soil test that could accurately predict nutrient availability.

To date, DGT technology has only been designed for separate assessment of anionic and cationic species in waters or soils typically at concentrations characteristic of highly contaminated systems. In this study a new mixed binding gel (MBL) was developed capable of simultaneous assessment of cations and anions in a single assay at concentrations more representative of uncontaminated agricultural soils, sediments and waters. The MBL has the potential to eliminate measurement errors associated with very fine spatial scale changes in element concentrations in these environments.

The MBL consisted of ferrihydrite and Chelex-100 cation exchange resin combined together in a binding gel. Results from the MBL were comparable to experiments performed using individual Chelex gels and ferrihydrite gels that have been shown to work successfully for DGT methodology. To facilitate combined analysis of P and cations by ICP-MS, HCl (1 M) was used for gel elution to minimise interferences from $^{14}N^{16}OH$ or $^{15}N^{16}O$ on ^{31}P. All elements tested (Cd, Cu, Mn, Mo, P and Zn) were bound successfully to the MBL. DGT measurements obtained using the MBL on agricultural soils correlated well ($r^2 = 0.95$) with measurements obtained using pure Chelex and ferrihydrite binding layers. This suggests that the MBL could be used for simultaneous measurement of cationic and anionic element availability in soils.

Performance of the Diffusive Gradient in Thin Films (DGT) technique was compared with three other common testing methods (Colwell, Olsen, Resin) for available soil P in terms of the ability of each to predict wheat, canola, lupin and barley responsiveness to applied P on 21 Australian agricultural soils. DGT accurately predicted plant responsiveness in > 90 % of the soils used. In contrast the other soil testing methods failed to correctly predict plant response to P on numerous occasions. These observations reveal that the DGT technique with the newly developed MBL can predict plant available P on these soils with greater accuracy than other traditional soil P testing methods and could become a useful tool for predicting P fertilizer requirements.

The DGT method using the MBL was also used to test Zn deficiency thresholds for canola and wheat in a manufactured soil (acid washed sand). DGT successfully determined the threshold for Zn deficiency in this soil, overcoming detection limit issues usually accompanying such low levels of Zn. This method also provides that potential to assess other micronutrients (Mn, Cu) and with further modification potentially assess K.

Before DGT can become established as an alternative soil testing method, validation of the performance is required under field conditions. This study has shown that it out performs current common soil testing methods in glasshouse conditions but questions still remain if this will be reflected out in the field.

Declaration

This work contains no material which has been accepted for the award of any other degree or diploma in any university or other tertiary institution and, to the best of my knowledge and belief, contains no material previously published or written by another person except where due reference has been made in the text.

I give consent for this thesis, when deposited in the University Library, to be available for loan and photocopying.

Sean David Mason **Date**

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Abbreviations

A	Area (cm^2)
AAS	Atomic Adsorption Spectrometer
AEM	Anionic Exchange Membrane
Ag	Silver
Al	Aluminium
As	Arsenic
ASV	Anodic Stripping Voltammetry
Ba	Barium
Ca	Calcium
$CaCl_2$	Calcium Chloride
$CaCO_3$	Calcium Carbonate
Cd	Cadmium
C_{DGT}	Concentration DGT
C_{diff}	DGT interfacial concentration (diffusion only case)
C_E	Effective concentration (DGT)
C_e	Concentration of the eluted gel (DGT)
C_i	DGT interfacial concentration of labile analyte species
C_{ls}	Liable element pool on the solid phase
Cl	Chloride
cm	Centimetre
Co	Cobalt
$CoSO_4.7H_2O$	Cobalt Sulfate
CO_2	Carbon Dioxide
Cr	Chromium
CSIRO	Commonwealth Scientific Industrial and Research Organisation
C_{soln}	Soil solution concentration (diffusion-only case)
Cu	Copper
$CuSO_4.5H_2O$	Copper Sulfate
D	Diffusion gradient of element through the diffusive layer
DGT	Diffusive Gradients in Thin Films
DI	Deionised
DIFS	DGT Induced Fluxes in Sediments and Soils
D_o	Element diffusion coefficient in water
DOC	Dissolved Organic Carbon
dp	Density of soil particles (2.65 g cm^{-3})
Ds	Diffusion gradient of element through soil
DTPA	Diethylenetriamenepentaacetate acid
EC	Electrical Conductivity
ETDA	Ethylenedinitrilotetraacetic acid
F	Fluoride
F	Flux of analyte through diffusive and filter layers (DGT)
FA	Fluvic Acid
Fe	Iron
F_e	Elution factor (DGT)
FeSO4.7H2O	Iron Sulfate
g	Gram
GFAAS	Graphite Furnace Atomic Adsorption Spectrometer
h	Hour

H	Hydrogen
ha	Hectare
H_2SO_4	Sulfuric acid
H_3BO_3	Boric acid
H_3PO_4	Phosphoric acid
HCL	Hydrochloric acid
HCO_3-	Carbonate
Hg	Mercury
HNO_3	Nitatre
I	Intensity (soil solution concentration)
ICPMS	Inductively Coupled Plasma Mass Spectrometry
ICPOES	Inductively Coupled Plasma Optical Emission Spectrometry
IS	Ionic Strength
IUPAC	International Union of Pure and Applied Chemistry
K	Potassium
K_2SO_4	Potassium Sulfate
K_2PO_4	Potassium Phosphate
kg	Kilogram
l	Litre
M	Molar
m	Metre
M	Measured accumulated mass (DGT)
MBL	Mixed Binding Layer (DGT)
MDL	Method Detection Limit
Mg	Magnesium
$MgSO_4.7H_2O$	Magnesium Sulfate
mg	Milli-gram
$MgCl_2$	Magnesium Chloride
ml	Milli-litre
mM	Milli-molar
mm	Milli-metre
Mn	Manganese
MnO_2	Manganese Oxide
$MnSO_4.7H_2O$	Manganese Sulfate
Mo	Molybdenum
N	Nitrogen
Na	Sodium
NaCl	Sodium Chloride
$NaHCO_3$	Sodium Bicarbonate
$NaNO_3$	Sodium Nitrate
NaOH	Sodium Hydroxide
Na_2SO_4	Sodium Sulfate
ng	Nanno-gram
$(NH_4)_2SO_4$	Ammonium Sulfate
NH_4	Ammonium
NH_4F	Ammonium Fluoride
NH_4NO_3	Ammonium Nitrate
$(NH_4)_6Mo_7O_{24.}4H_2O$	Ammonium Molybdate
Ni	Nickel
NO_3	Nitrate
NO_3N	Nitrate-Nitrogen

O_2	Oxygen
P	Phosphorus
Pb	Lead
P_c	Particle concentration
Q	Quantity
QLD	Queensland
r	Correlation coefficient
r^2	Coefficient of determination for a fitted regression curve
R_{diff}	Ratio between C_{DGT} and C_E (DGT), calculated using 2D DIFS
S	Sulfur
S.A.	South Australia
SO4	Sulfate
Sr	Strontium
t	Time (secs) DGT
TDS	Total Dissolved Solids
TEMED	Tetramethylethylenediamine
µg	Micro-gram
µm	Micro-metre
µmol	Micro-molar
µS	Micro-Siemens
Ve	Volume of the acid added to elute the gel (DGT)
Vg	Volume of the binding layer (DGT)
VIC	Victoria
W	Watt
W.A.	Western Australia
WHAM	Windermere Humic Aqueous Model
WHC	Water Holding Capacity
Zn	Zinc
$ZnCl_2$	Zinc Chloride
$ZnSO_4.7H_2O$	Zinc Sulfate
Φ	Porosity
Δg	Diffusive layer thickness

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