Development of the diffusive gradients in thin films (DGT) technique for plant available potassium measurement in Australian soils

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of the requirement for the degree of Doctor of Philosophy

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ABSTRACT

Potassium (K) is an essential plant macronutrient and the most abundant cation found in plants. Except for nitrogen (N), K is taken up by plants more than any other nutrient from the soil (Havlin et al. 2005). Due to the complexity of the plant K uptake process, which is affected by multiple factors, the traditional soil K testing methods (e.g. $CaCl_2$ K, Colwell K, NH_4OAc K, etc.) have generally failed to provide an accurate indication of the amount of K fertilizer should be applied before planting. Beyond measurements of bioavailable fractions of trace elements, the relatively new diffusive gradients in thin films (DGT) method has successfully predicted plant-available phosphorus (P) in agricultural soils. As the main mechanism of K uptake by plants is by diffusion, which is the same mechanism of P uptake by plants, it is likely that the DGT could provide an accurate prediction of plant K requirements.

The DGT K method has been improved to enable measurement of both plant-available P and K in soils by using a new mixed Amberlite and ferrihydrite (AMF) gel. Compared to the resin gel used by Tandy et al. (2012), the MAF gel has improved properties in terms of Amberlite distribution resulting in a flat shape, which avoids the difference in length of K^+ diffusion pathways caused by unevenly-distributed Amberlite particles in the gel and aids in the process of preparing the DGT devices. With the new resin gel, it was revealed that the DGT method can be used at longer deployment times (>2 h) and was capable of measuring solution concentrations of K larger than 16 mg L^{-1} - limitations which were reported by Tandy et al. (2012). It was also the first time that the diffusion coefficient of K through the diffusive gel was fully investigated in the presence of competing cations (e.g. Ca^{2+}, Mg^{2+} and NH_4^+).

Since the MAF gel incorporates ferrihydrite, which is traditionally used for P measurement using the DGT method, the MAF gel was shown to have the ability to measure both P and K in solution and in soils, compared with the traditional gel containing ferrihydrite alone. Besides having the ability to take up K, the MAF gel also has the ability to bind calcium (Ca) and magnesium (Mg) from solution. With the measurement of elution and uptake efficiencies of the MAF gel for Ca and Mg and the diffusion coefficients of Ca and Mg through the diffusive gel, the DGT method can also be used to measure the available of Ca and Mg in solution and soil environments.

Due to higher affinity of the MAF gel for Ca and Mg compared to K, measurement of available K in soil using the DGT method is mainly restricted by Ca, the main competing cation present in agricultural soil solutions. In some scenarios, high Ca concentrations in soils mean that shorter deployment times must be used or else measurements of K are affected. Larger effects of deployment time on the C_{DGT} of K were observed at shorter deployment times. The effects of thickness of the diffusive gel on the C_{DGT} of K were found to be inconsistent across soils.

Finally the accuracy of the DGT K method and the traditional extraction methods for K were compared in terms of predicting wheat growth to K application in soils at two different root densities in a glasshouse trial. For predicting wheat relative yield, the Colwell K and NH_4OAc K methods were more accurate compared than the DGT and $CaCl_2$ K methods at low root densities, which is the situation most relevant to field conditions. The ability of the DGT K method to predict plant response to K varied with root density, and was poor at low root densities. However, the DGT K method was a good predictor of wheat tissue K concentrations irrespective of root density ($R^2 \geq 0.84$). Further investigation showed that the increases in concentrations of K measured by the DGT method as a function of rate of K

fertilizer application were highly (inversely) correlated to the potassium buffering abilities (KBA) of the soils (R^2=0.96). KBA may be a good predictor of soils that are potentially prone to depletion of available K and susceptibility to deficiency, as soils with low KBA have a reduced ability to resupply soil solution K pools in response to K removal by plant roots.

The DGT K method is not recommended for adoption as a soil test K method for wheat before further evaluation of the performance using crop responses to K in field conditions. There is room for further improvement of the method to measure more strongly bound K in soil which appears to contribute to crop K nutrition, by changes to the binding gel and the diffusive gel in order to obtain more selective uptake of K by the binding gel and potentially change the transport of K through the diffusive gel. As K uptake varies between plant species, the ability of the DGT K method to predict K requirements by other crop types also requires evaluation.

DECLARATION

I certify that this work contains no material which has been accepted for the award of any other degree or diploma in my name, 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. In addition, I certify that no part of this work will, in the future, be used in a submission in my name, for any other degree or diploma in any university or other tertiary institution without the prior approval of the University of Adelaide and where applicable, any partner institution responsible for the joint-award of this degree.

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LIST OF PUBLICATIONS

Zhang Y, Mason S, McNeill A, McLaughlin MJ (2013) Optimization of the diffusive gradients in thin films (DGT) method for simultaneous assay of potassium and plant-available phosphorus in soils. Talanta 113: 123-129.

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STATEMENT OF AUTHORSHIP

Components of the research described in this thesis have been published or will be submitted for publication (as listed below). The contribution of each author to these works is described below.

Chapter 2: Talanta, 2013. **113**: 123-129.
Chapter 3: Analytica Chimica Acta, 2014. **842**: 27-34.
Chapter 5: To be submited
Chapter 6: To be submited

Zhang, Y. (Candidate)

Experimental development, performed analysis on all samples, data analysis and critical interpretation, wrote the manuscript.
I hereby certify that the statement of contribution is accurate.

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Mason, S.

Supervised development of work, data analysis and interpretation, reviewed and edited the manuscript.
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Nachimuthu, G.

Experimental development, performed analysis data and interpretation, reviewed the manuscript.

I hereby certify that the statement of contribution is accurate.

Signed Date 28/01/2015

STRUCTURE OF THE THESIS

This thesis is presented as a combination of papers that have been published and paper drafts in publication style.

Chapter 1 provides an overview of the literature on roles K in plant growth, K status in soils, traditional K test methods, the theory of the DGT technique and also the research aims.

Chapter 2 comprises a paper that has been published in *Talanta*. This chapter describes the optimization of the DGT method for simultaneous assay of K and plant-available P in soils, focusing on the improvement of the resin gel.

Chapter 3 comprises a paper that has been published in *Analytica Chimica Acta.* This chapter invesitigates the effects of competing cations on K uptake by the resin gel and initial C_{DGT} of K measurement on soil test.

Chapter 4 comprises a paper draft that will be submitted to *Plant and Soil*. This chapter invesitigates the effects of deployment time and thickness of the diffusive gel on measured C_{DGT} of Ca, K, Mg and P.

Chapter 5 comprises a paper draft that will be submitted to *Plant and Soil*. This chapter compares the accuracy of different soil K test methods in predicting wheat response to K application under two root densities in glasshouse conditions.

Chapter 6 comprises a paper draft that will be submitted to *Plant and Soil*. This chapter assesses the KBA and soil test values and assesses the ability of the NST 3.0 modelling in predicting wheat K uptake under different root densities.

Chapter 7 provides a synthesis of the findings contained in this thesis and includes recommendations for future work.

Appendices section comprises four sections of experimetns in terms of DGT K method improvement and a photo page describing the main experiments carried out through out the thesis.