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

A thesis submitted to The University of Adelaide in fulfilment
of the requirement for the degree of Doctor of Philosophy

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## TABLE OF CONTENTS

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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

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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.

Zhang Y, Mason S, McNeill A, McLaughlin MJ (2014) Application of the diffusive gradients in thin films technique for potassium measurement in agricultural soils: Effects of competing cations on potassium uptake by the resin gel. Anal Chim Acta 842: 27-34.

## 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.
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Chapter 6: To be submited

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

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

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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.

# CHAPTER 1

## Review of the literature

## 1. Introduction

Potassium (K) is an essential macronutrient for plant growth. Potassium deficiency is becoming a problem for crop production in many countries, especially in some developing countries (Manning 2010). Occurrences of K deficiency have also been reported in some cropping areas in Australia (Bell et al. 2009; Brennan and Bolland 2009; Wong et al. 2001). An accurate soil testing method for predicting plant K requirement before seeding has become increasingly important in limiting crop yield losses due to K deficiency and for maximising K fertilizer efficiency. Due to the complexity of K availability/accessibility to plant roots, the accuracy of the most commonly used extraction methods has been reported to be poor, specifically to soil-type dependent (Brennan and Bell 2013; Gourley et al. 2007). Therefore, an accurate soil K test method for predicting crop K requirements has become more important as K fertilizer prices increase and with the development of precision agriculture.

The diffusive gradients in thin films (DGT) technique is relatively a new method for measurement of the bioavailable fraction of an element in water, sediments and soils. Greater accuracy was also found in predicting plant phosphorus (P) uptake response to P application using the DGT method compared to traditioanl extraction methods (Mason et al. 2010; Menzies et al. 2005; Speirs et al. 2013). As the basis of the DGT method is diffusion which is the same mechanism whereby plant roots take up K from soils, it appears to be a feasible tool for predicting plant-available K in soils.

This review covers role of K in plant growth, K status in soils, traditional soil K testing methods and the basic theory of the DGT technique. In the following chapters, a series of experiments were carried out to investigate the application of the DGT method for K testing in terms of optimization of the resin gel, exploration of effects of competing cations on K

uptake by the DGT device, exploration of the effects of deployment time and thickness of the diffusive gel on K uptake by the DGT device, comparing the accuracy of the DGT K method and traditional extraction methods in predicting wheat responses to K application and discussing the potassium buffering ability (KBA) of soils and its effect on soil tests for available K in soil.

## 2. Role of K in plant growth

### 2.1. Functions of K in plant physiology

Potassium is involved in many essential physiological activities in plants. It is reported that the activation of more than 60 different enzymes are either directly or indirectly controlled or stimulated by K (Marschner 1995). The abundance of K ions in cytosols and chloroplasts balances the charge of soluble and insoluble anions, thereby stabilizing the pH between 7 and 8, which is important for most enzyme activation (Hawkesford et al. 2012). Peoples and Koch (1979) reported that the synthesis of the enzyme for chloroplast protein is very sensitive to K. As the chloroplast is the main location where photosynthesis occurs, insufficient K restricts photosynthesis in plant leaves to varying degrees (Hawkesford et al. 2012). Potassium can increase the rate of catalytic reactions by inducing conformational changes of enzymes (Envans and Wildes 1971). Adequate K promotes transport of photosynthates in phloem by maintaining a high pH in the sieve tubes for sucrose loading and contribution to the osmotic potential, the drivers of photosynthate transport (Hawkesford et al. 2012).

Potassium also contributes to cell extension and division. Potassium accumulation can stabilize solution pH in the apoplast and the cytoplasm, and increase the osmotic potential in the vacuoles, which is the first step for cell extension and division (Hawkesford et al. 2012). In addition, K controls the opening and closing of stomatal guard cells, thereby affecting the

regulation of plant water status and $CO_2$ absorption (Fischer and Hsiao 1968). This function is extremely important for plants growing in soils without sufficient soil moisture.

### 2.2. Effects of K deficiency on plant growth

Plant growth is highly dependent on plant tissue K concentrations. Rao (1986) reported that deficiency of K in plants restricts leaf growth, which in turn results in reduced growth, plant dry matter and grain yield. Glasshouse studies have shown that K deficiency in cotton can lead to smaller organs at sites away from the main stem source leaves e.g. tips, leaves, flower etc. (Gerardeaux et al. 2010). Potassium deficiency can lead to reduced value or quality in crop and fruit products (Pettigrew 2008), for example a decreased wheat seed size or an increased bitterness in lupins due to accumulation of alkaloids (Wong 2001). It is also reported that K deficiency leads to a higher population of soybean aphid in the midwest United States because of the increased percentage of asparagine in the phloem of soybean caused by K deficiency, which is important for aphid nutrition (Walter and DiFonzo 2007). On the contrary, it is generally accepted that high K status in crops decreases the incidence of diseases and pests (Perrenoud 199; Prabhu et al. 2007; Bergmann 1992). Mengel and Kirkby (2001) found that plants have better hydrated tissues than those suffering K deficiencies. Sufficient K can also increase the frost resistance of potato (Grewal 1980) and alleviate Na toxicity (Kopittke 2012). Consequently, sufficient available K in soils for plant uptake is the prerequisite to guarantee sufficient K uptake by plants.

## 3. Potassium status of agricultural soils

### 3.1. Potassium deficiency in agricultural areas

Potassium was actually defined as “the forgotten element” early in 1997 (Krauss 1997), but scientific awareness of the forgotten element has not been improved, even in recent years. Potassium deficiency has increasingly become a problem in agriculture in many countries,

particularly in some developing countries (Manning 2010). Areas with coarse sandy soils or soils with a high organic matter content are prone to K deficiency (Öborn et al. 2005), since low mineral K content is normally associated with soils that have a high organic matter content (Barber 1995). Tan et al. (2012) reported that soils in North China were seriously deficient in K due to non-application of K fertilizer. Rengel and Damon (2008) found that three quarters of the paddy soils in China and two thirds of the wheat belt in southern Australia were deficient in K, and leaching of K, especially in sandy soils, contributed to a reduction of K levels. Occurrences of K deficiency in wheat have been found in Western Australia due to the nature of the soils (sandy) and depletion of K (Wong et al. 2001). Brennan and Bolland (2009) identified several occurrences of K deficiency in wheat and canola field trials in southwest Australia. In the same year, Bell et al. (2009) reported a decline in plant-available K reserves in northern Australian grain cropping areas.

### 3.2. Insufficient K inputs to meet demand

Compared to other macronutrients, especially nitrogen (N) and phosphorus (P), little attention has been paid to K nutrition in crop productivity over the last few decades. Supporting evidence can be found through data on low fertiliser sales in Australia during these years (Figure 1.1). Potassium fertilizer sales are approximately half those of P, however, on average crops remove more K from the soil through grain uptake than P (Table 1.1). Consequently, in many parts of Australia we are mining K from the soil and there is a need for scientific awareness of these problems. Dobermann et al. (1998) estimated that the total annual K needed for irrigated rice in Asia will increase from $0.9\text{-}1.2\times10^6$ t in 1993 to $9\text{-}15\times10^6$ t in 2025 according to projected rice production requirements. This suggests that there are potential problems worldwide for increase in occurrences of K deficiency.

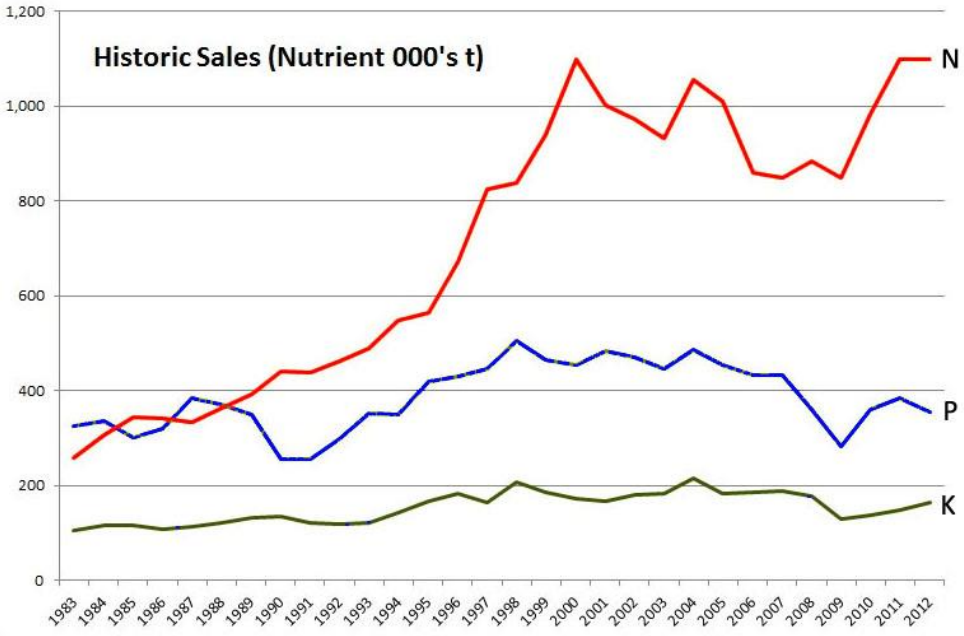


**Figure 1.1** Historic nutrients sales in Australian agriculture (kt) (FIFA 2013).

**Table 1.1** Nutrient removal by different agricultural products (Summit Fertilizers).

| Product | N | P | K | S | Ca | Mg |
|---|---|---|---|---|---|---|
| | kg per tonne | | | | | |
| Wheat | 23 | 3 | 4 | 1.4 | 0.33 | 0.93 |
| Barley | 20 | 2.9 | 4.4 | 1.1 | 0.3 | 1.08 |
| Oats | 16 | 3 | 4 | 1.5 | 0.5 | 1.0 |
| Canola | 40 | 6.5 | 9.2 | 9.8 | 4.1 | 4.0 |
| Lupins | 51 | 3.8 | 8.8 | 3.1 | 1.7 | 1.7 |
| Chickpeas | 34 | 3.8 | 8.9 | 1.8 | 1.1 | 1.2 |
| Faba Beans | 39 | 3.8 | 9.8 | 1.4 | 1.1 | 1.0 |
| Field Peas | 37 | 4.0 | 8.2 | 2.0 | 0.7 | 1.2 |
| Hay | 20 | 2.0 | 25 | 2.0 | 0.5 | 1.1 |
| Milk | 5.7 | 0.95 | 1.4 | 0.3 | 1.2 | 0.12 |
| Greasy Wool | 170 | 0.26 | 15.8 | 28.5 | 1.2 | 0.3 |
| Sheep - Live | 34 | 7.0 | 2.3 | 4.0 | 14.4 | 0.4 |

3.3. Disadvantage of gene research for maximizing plant growth

Scientists have made progress in plant breeding in terms of obtaining improved cultivars capable of survival under K deficiency. Woodend and Glass (1993) found that significant differences in dry matter and K use efficiency were observed among different genotypes of wheat. Gerloff (1977) reported that K-efficient genotypes have good adaptation to K-limiting conditions. It is also reported that dry weight of cotton cultivars with high K efficiency was

155% higher than that with low K efficiency genotypes, even when similar dry matter yields were obtained in K-sufficient solutions (Yang et al. 2011). The new cultivar with higher nutrient uptake efficiency is, to a large extent, due to an increase in root size. Gamuyao et al. (2012) identified a gene acting as a root enhancer in rice at the early stages of growth, thereby allowing the plant to take up more P and other nutrients. While plant breeding for improved genotypes does assist to identify plants that can take up more K from soils, with continued removal of K from soils without sufficient input, K deficiency will become an increasing problem. Therefore, the effective and most sustainable way to address the problem of K deficiency in soils is to still compensate the soil with moderate fertiliser K applications under the guidance of accurate soil testing. Therefore, it is a priority that attention should be paid to correcting the imbalance between K input and output in agricultural production areas.

## 4. Potassium balances in soil systems

### 4.1. Potassium forms in soils

There are four main operationally-defined pools of K in soils, soluble K, exchangeable K, slowly exchangeable K (exchangeable K or fixed K) and structural K (mineral K). Specifically, solution K is the free $K^+$ dissolved in soil solution; exchangeable K is weakly bound to exchange sites on the soil solid phase; slowly exchangeable K mainly refers to K strongly bound on exchange sites or trapped between interlayers of clay minerals; and mineral K refers to K in crystalline structure of feldspars, clay minerals and micas (Barber 1995; Huang et al. 2012).

Potassium movement in the soil-plant system can be depicted as in Figure 1.2. Different forms of K can move from one pool to another, but it is unlikely that equilibrium between pools ever exists due to plant removal of K and additions of K in fertilizer. Mineral K can dissolve into exchangeable K forms and slowly exchangeable K, conversely exchangeable K

and slowly exchangeable K pools cannot be converted back to mineral K, as K does not form sparingly soluble precipitates in soils. The remaining pools of K, namely solution K, exchangeable K and slowly exchangeable K can transfer between each other bi-directionally.

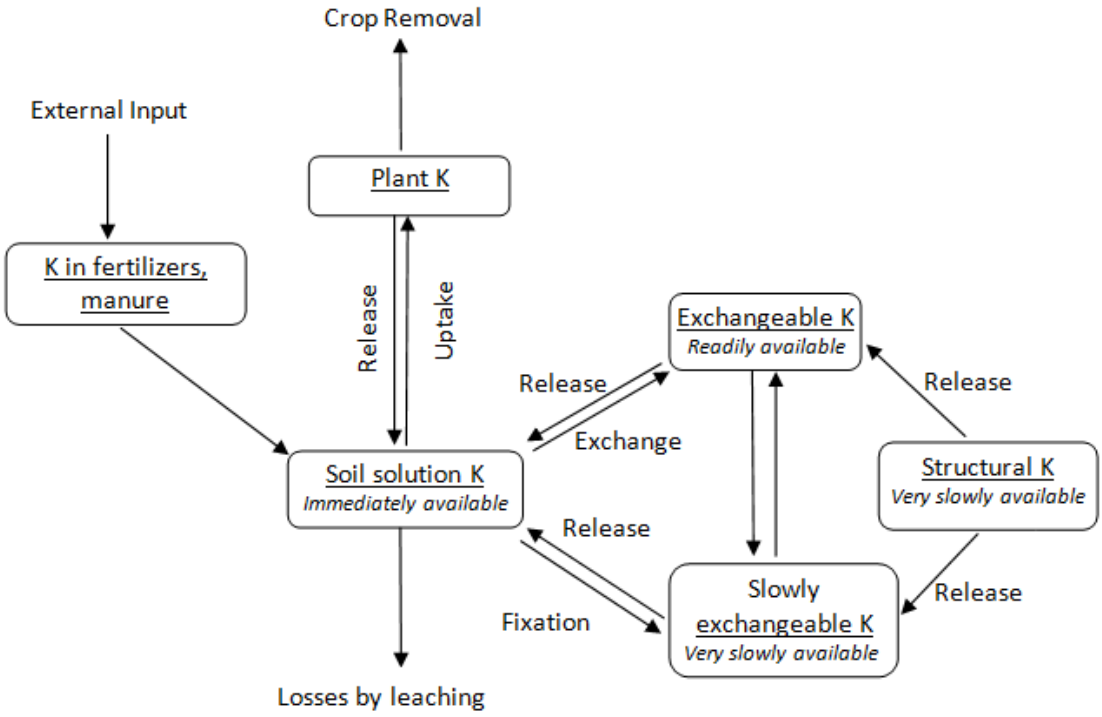


**Figure 1.2** Diagram of main processes of the K cycle in soils, modified from Syers (2003).

4.2. Potassium balance in the soil-plant system

The transfer of K between any two pools can be changed by a range of processes. Potassium can be removed from the soil-plant system by leaching of K through the soil profile as mentioned above. When soluble K moves to deeper soil depths or to the water table it can become inaccessible for plant uptake. Potassium can also be removed from the soil system at harvest time in the above ground part of the plants, especially when the residual stubble is not returned back into the soil (e.g. fodder hay). To correct for the removal, sources of K can also be added into the soil-plant system as fertilizers, plant ashes, plant residues and manure. Therefore there is an intrinsic balance between the inputs and outputs of K in the soil-plant system along with transitional changes between the different forms of K as depicted in Figure

1.2, depending on soil fertility management procedures such as product removal, stubble treatment, grain, hay pasture etc.

4.3. Plant available K

Higher plants take up K from soil solution. It is reported that soluble K accounts for 5% of the total plant demand at any one time (McLean and Watson 1985). Potassium loss from soil solution has to be replenished by exchangeable K and slowly exchangeable K sources in soils or K fertilization (Simard and Zizka 1994). The replenishment of K from the exchangeable K pool is usually more rapid than that from the slowly exchangeable K pool. Slowly exchangeable K can become available when exchangeable K and solution K are decreased (Sparks et al. 1980). Although the release of slowly exchangeable K is slow, it has also been suggested, from a K exhaustion experiment, that slowly exchangeable K accounts for a large proportion of the total K taken up by plants (Dai and Li 1997). Marschner (2012) reported that plants grown in the field do not uniformly take up K, even from densely rooted topsoils, due to poor mobility of K in the bulk soil: plants can take up a higher proportion of slowly exchangeable K near the root surface but readily exchangeable K in bulk soil that is not in close proximity to roots is not used. Where there was insufficient exchangeable K for plants, mineral-bound K also contributed to plant available K which was mobilised in the presence of root exudates including oxalic acid, malic acid, tartaric acid or some organic acids (Wang 2009). Similarly, Moody and Bell (2006) also reported that mineral K (or structural K) was independent of the exchangeable K pool along with the fixed K pool (also called slowly exchangeable K), but it correlated well with solution K if solution K was exhausted in the soil (Figure 1.3). It can be concluded that when soil solution K is low, structural K can be an important source of plant available K.

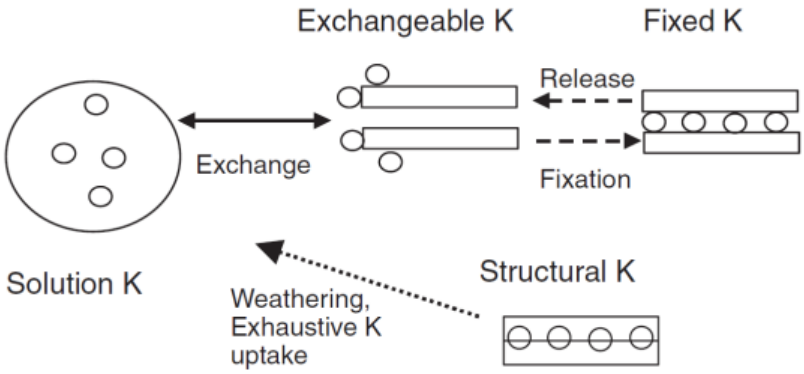


**Figure 1.3** Interactions between the various soil K pools (Moody and Bell 2006).

## 5. Plant K uptake

### 5.1. Nutrients uptake by plants in relation to K

Plant nutrient uptake by roots is facilitated by three different mechanisms: 1) root interception, 2) mass flow and 3) nutrient diffusion (Figure 1.4). Root interception refers to when plant roots grow in bulk soils; nutrients are taken up by direct contact of the plant root surface with nutrients on the soil surface. Therefore, the contribution of root interception to plant nutrient uptake is, to a large extent, dependent on root size and morphology. Mass flow is caused by plant transpiration. When water is taken up via the root surface, the moisture potential near the plant root is lowered. Consequently water from bulk soil moves to the root surface, bringing nutrients in solution to the root surface at the same time. As a result, water use by different plant species, climate and soil water content are the main factors affecting the contribution of mass flow to plant nutrient uptake. Mass flow provides plants with Ca and Mg to a greater extent than P and K (Barber et al. 1963; Jones 2012). Nutrient diffusion occurs when mass flow and root interception cannot supply a plant with sufficient amounts of any nutrient, resulting in a lowered nutrient concentration at the root surface. Therefore, nutrient in soil solution always diffuses towards the root surface, establishing a concentration gradient to the root (Malcolm et al. 1996).

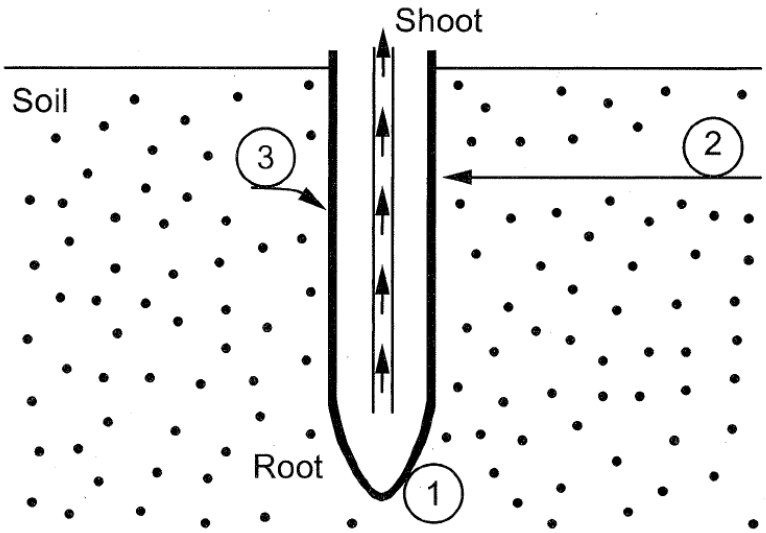


**Figure 1.4** Schematic presentation of the movement of elements to the root surface of soil-grown plants. (1) Root interception: soil volume displaced by roots. (2) Mass flow: transport of soil solution along the water potential gradient (driven by transpiration). (3) Diffusion: element transport along a concentration gradient. ● =available nutrients (as determined, e.g. by soil testing) (Marschner and Rengel 2012).

## 5.2. Plant acquisition of K from soils

Generally the concentration of $K^+$ in soil solution is so low that mass flow cannot provide the plant root with sufficient K. Among the mechanisms of nutrient uptake by plant roots, diffusion is identified to be the main one for plant root K uptake (Barber 1995; Barber et al. 1963; Mills et al. 1996). Baligar (1985) reported diffusion contribution to K uptake by plants was 99% for corn (20 days growth) and 96% for wheat (25 days growth), respectively.

## 5.3. Factors affecting K availability or accessibility by plants

Potassium availability and/or its accessibility to plant roots vary greatly and are dependent on many different factors. The availability of a nutrient in a soil is mainly dependent on the rate at which that nutrient moves through the soil to the plant root surface (Barber 1962). The following is a discussion of the main factors which affect the process of K uptake by plants.

### *5.3.1. Plant root*

Because most nutrients are taken up by plant roots, root size and morphology have a close relationship with nutrient uptake. Silberbush and Barber (1983) reported that plant K uptake

is mostly associated with root surface area. Similarly, Gamuyao et al. (2012) improved P uptake efficiency of rice by genotypic modification in terms of obtaining larger root mass. Vandamme et al. (2013) also found that P uptake by soybean was to a large extent affected by root length and density. These factors might be important for K as well. Since K only diffuses within a few millimetres around a plant root, K ions further away have no effect on K uptake by plant roots (Havlin et al. 1999). Consequently, a larger root system in the bulk soil allows the plant to get access to more K in soils.

### *5.3.2. Soil texture*

Compared to sandy and loamy soil types, clay soils with higher clay contents and therefore larger surface areas play an important role in the retention of K and other cations. Ajiboye and Ogunwale (2013) measured soil K in each soil mineral fraction (sand, loam and clay) and concluded that clay fractions had the highest soil testing values using a wide range of soil testing methods. Munn et al. (1976) reported that clay, silt and sand contributed to 30-74%, 24-56% and 3-21% of the total K release from each fraction, respectively.

### *5.3.3. Competing cations in soil solution and soil CEC*

Antagonistic interactions between $K^+$ and $Ca^{2+}$ and $Mg^{2+}$ have been reported widely, K uptake by plants can be affected in the presence of these competing cations (Fageria 1983; Johansen et al. 1968). More specifically, Fageria (1983) reported that K uptake by rice plants was stimulated at low $Ca^{2+}$ concentration in a solution cultivation experiment, but restricted at high $Ca^{2+}$ concentration. Jones (2012) also found that excessive Ca in soils could cause a deficiency of K in plants. In addition, uptake of $NH_4^+$ was also found to reduce K uptake by some plants (Jones 2012).

Soil cation exchange capacity (CEC) indicates the ability of soil to bind cations from soil solution. Usually, the higher the CEC (and given similar soil solution K concentrations), the

greater the capacity of a soil to supply plants with K (Glendinning 1999). McLean (1976) argued that when soil CEC was higher, more Ca would be present in soil solution and result in a relatively lower proportion of K in solution which is available to plants.

### *5.3.4. Soil water content*

Soil water is required for K to diffuse towards the plant root surface. Low soil water content results in rapid depletion of available K in soils near the root surface, generating steep concentration gradients and reducing the volume of the soil that supplies available K. On the contrary, high soil water content enables a gentle gradient of K that forms in a larger volume of soil, but with a relatively lower concentration. Furthermore, low soil water content also restricts the growth of roots and therefore the amount of soil explored for K uptake (Kuchenbuch et al. 1986). Thus, neither low soil water content nor high soil water content is necessarily better for plants to utilise K sources.

### *5.3.5. Soil aeration*

Poor soil aeration has been shown to inhibit the ability of plant roots to absorb K by hindering aerobic respiration (Glendinning 1999). In addition, the process of releasing mineral K from the lattice is restrained by the reduced activity of aerobic microorganisms caused by poor aeration conditions in the soil.

### *5.3.6. Soil temperature*

Soil temperature affects the transfer between the four designated pools of K in soil. The lower the temperature, the slower $K^+$ diffuses through the soil solution. A lower enzyme activation by plant roots is also associated with a lower soil temperature, resulting in a poor ability of the plant root to take up K (Barber 1995).

*5.3.7. Potassium fertilizer application methods*

Banding K fertilizer below the seed row has been recommended to be a better method for fertilizer application in dryland cropping system in South Australian cereals (Wilhelm and White 2004, Figure 1.5). A broadcasting application method was reported to be poorly effective due to dry weather after application. This study also indicated that K was important for cereal growth mainly during the early stages, as shown by the distinct yield differences between treatments applied at tillering compared to treatments applied at or before seeding. It is also important to adjust the amount of K fertilizer according to the K buffering ability of soils, as sandy soils are prone to K loss due to less binding sites on the soil solid phase.

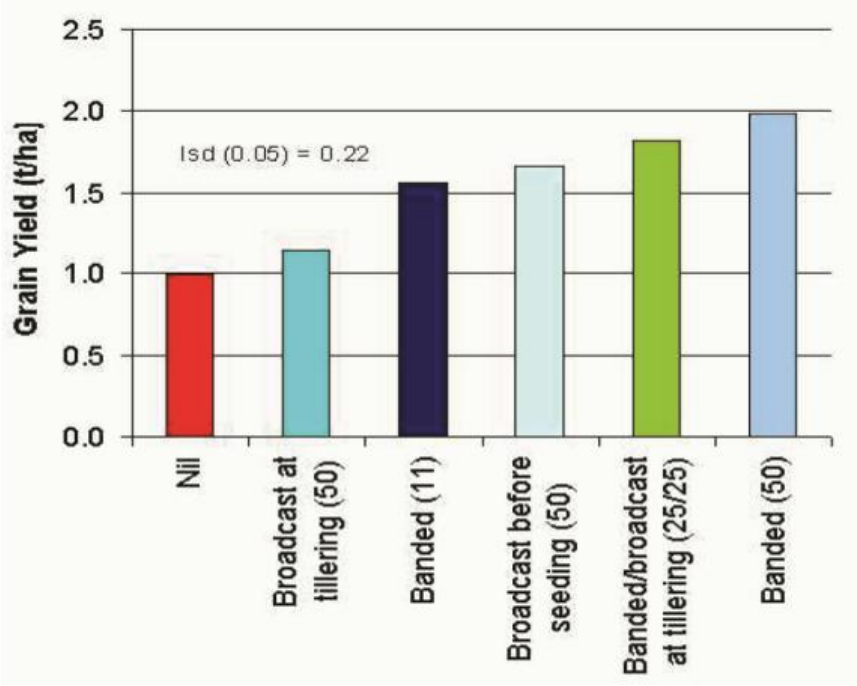


**Figure 1.5** Effects of K application methods on grain yield (Wilhelm and White 2004).

## 6. Traditional soil K testing methods

6.1. Soil K testing methods

To achieve precise agricultural management, a soil test is the necessary first step in making important decisions, such as soil fertility assessment and fertilizer recommendations. The rationale of these soil K tests is that all extracted K should be potentially available to the

plant. The common practice for determining the relative success of a soil test is to show its ability to predict crop responses when the appropriate nutrient is applied. A response is typically measured by the percentage of maximum yield, which is defined as the yield without nutrient application divided by maximum yield when the non-limiting nutrient is applied. At 90% of the maximum (economic) yield, a critical soil test value can be established by calculating the x- intercept value of the relationship between soil test results and crop (economic) response. If the relative yield indicated by soil testing result is less than 90%, a certain amount of fertilizer is needed, which is the minimum requirement in terms of crop yield (Chapman et al. 1992; Holford and Cullis 1985; Holford et al. 1985).

Currently the most common methods for measuring available K in soil are solution K methods and extraction methods: soil solution K determines K in soil solution usually obtained by Rhizon$^{TM}$ samplers (Knight et al. 1998; Song et al. 2003) or centrifuge method (McLaughlin et al. 1997); extraction methods determine the amount of K exchanged with the cation from a chemical solution, which is regarded as the exchangeable K. Houba et al. (1990) proposed 0.01 M $CaCl_2$ as an extractant for K testing of soils in a soil to solution ratio of 1:10 (W/V) which could be used for practical diagnostic purposes. Grimme and Németh (1978) reported that the quantity of K extracted by 0.013 M $CaCl_2$ correlated well with solution K and with crop response. The comparatively low concentration of Ca in the $CaCl_2$ extraction method compared to that in other chemical extraction methods and high correlation with solution K indicates that exchanging of $Ca^{2+}$ with $K^+$ from soil solid phase is not the main mechanism of action of this test, but solution extraction. Therefore, the $CaCl_2$ method is categorised more close to a "solution K method", rather than an exchangeable K method. $NaHCO_3$ (Colwell 1963) and $NH_4OAc$ (Spencer and Govaars 1982, Rayment and Higginson 1992) have also been widely used for extracting K from soils but cation concentrations are higher so solution K and weakly-exchangeable K are simultaneously

extracted. Scott et al. (1960) developed the method of using sodium tetraphenyl borate ($NaBPh_4$) as an extractant to test available K trapped inside soil colloids and minerals (non-exchangeable K). Later, a series of modified $NaBPh_4$ methods were developed to test available K in soils. For example, Cox (1996) suggested that $NaBPh_4$ could extract most of the non-exchangeable K in soils. To date, there have been many different extraction methods used in research and agricultural practice (Table 1.2).

**Table 1.2** Common soil K extraction methods used in Australia, modified from (Peverill et al. 1999).

| Common name | Extractant | Concentration/ pH | Soil/solution ratio | Extraction time | Reference |
|---|---|---|---|---|---|
| *Exchangeable K* | | | | | |
| | $NH_4Cl$ | 1 M, pH 7 | 1:20 | 1 h | Rayment and Higginson 1992 (method 15A1,15A2) |
| | $NH_4Cl$[A] | 1 M, pH 8.5 | 1:20 | Leached | Rayment and Higginson 1992 (method 15C1) |
| | $NH_4OAc$[A] | 1 M, pH 7 | 1:50 | Leached | Rayment and Higginson 1992 (method 15D1) |
| | $NH_4OAc$ | 1 M, pH 7 | 1:10 | 30 m | Spencer and Govaars 1982 |
| | $BaCl_2$ | 0.025 M, pH 7 | 1:100 | 16 h | Spencer and Govaars 1982 |
| | $BaCl_2$<br>$NH_4Cl$ | 0.1 M<br>0.1 M, pH 7 | 1:100 | 16 h | Rayment and Higginson 1992 (method 15E1) |
| *Extractable K* | | | | | |
| Colwell K | $NaHCO_3$ | 0.5 M, pH8.5 | 1:50 | 16 h | Colwell 1963 |
| Skene K | HCl | 0.05 M | 1:20 | 1 h | Skene 1956 |
| | HCl | 0.05 M | 1:10 | 16 h, 16 rpm | Haysom 1982 |
| | HCl | 0.1 M | 1:40 | 4 h | Cox 1974 |
| Nitric acid soluble K | $HNO_3$ | | | | Pratt 1951 |
| Non-exchangeable extractable K (NEAK) | Resin extractable K/ $BaCl_2$ exch.K | | 1:5 | 20 h (at 80 $^oC$) | Waddy and Vimpany 1970 |
| Resin extractable K | Cation exchange resin | | | | McLaughlin et al. 1994 |
| Soil solution K | Saturated paste extract | | approx. 20g wet to saturation | Equilibrated for 24 h | Rayment and Higginson 1992 (method 2D1) |
| | $CaCl_2$ | 0.01 M | 1:10 | 2 h | Salomon 1998 |
| Total K X-ray fluorescent spectrometry | pressed powder | | | | Rayment and Higginson 1992 (method 17A1) |

[A] These procedures involve pre-treatment for soluble salts using alcohol (Rayment and Higginson 1992).

6.2. Problems with traditional methods

Currently used methods for testing available K in soils all potentially have common problems: namely, using different agents and/or different concentrations, different extraction temperatures and/or different soil to water ratios to those found in soil during plant growth and K uptake. Firstly, extraction methods can cause reaction surfaces to be exposed to solution by mutual abrasion of soil particles, this exposing more surfaces than plant roots can access (Barrow 2008). Therefore, soil structure, soil chemical components and the affinity of soil colloids for nutrient elements change when the extractant is added to soil. Based on these changed soil properties, it is highly likely that the amount of K (and other elements) extracted by these traditional methods is different to the inherent availability of K in the soil. Secondly, the soil to water/extractant ratio is also much smaller compared to the soil water conditions under which the plants are grown. When K is extracted from soils, generally the extraction is performed in a relatively large amount of extracting solution, thereby diluting the salt in soils, dispersing soil colloids and changing the solution pH. Soil pH has a profound impact on the availability of plant nutrients (Figure 1.6). The availability of K declines sharply when the pH is below 6. It appears that the availability of K is not affected by soil pH values greater than 6. However, the concentrations of the competing ions calcium and magnesium generally increase at higher soil pH values, thereby inhibiting K uptake by plants. The fixed pH used in many extraction methods differs from the natural pH status found under field conditions and therefore the soil chemical factors that drive K availability are altered. All these factors could contribute to the inaccuracy of the results gained by traditional extraction methods.

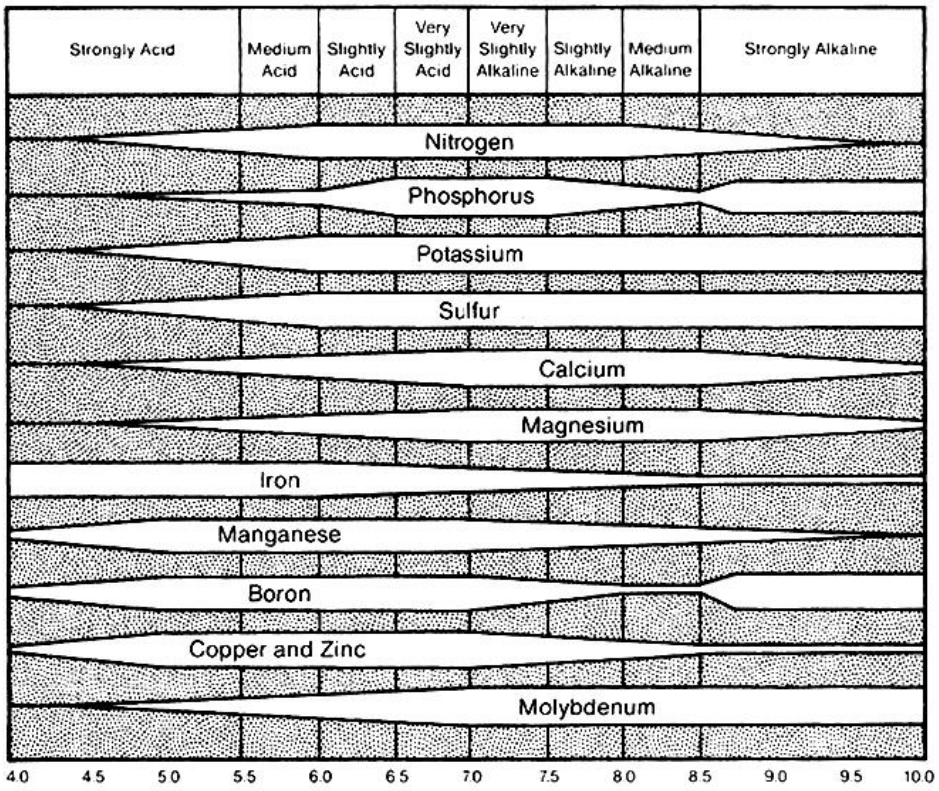


**Figure 1.6** Availability of some essential elements as influenced by soil acidity or alkalinity (McMahon et al. 2007).

Practically, the inaccuracy of traditional soil tests is highlighted in the report by Gourley et al. (2007). Colwell K (extracted by $NaHCO_3$) values were segregated by soil type (namely sandy soils, sandy loams, sandy clay loams and clay loams) and each was related to pasture response to K application (Figure 1.7). This process produced different critical soil test values (soil K value at 95% of maximum yield) for each soil type. However, based on the 95% maximum yield, there is a large range of soil test values where both responsive and non-responsive sites occur in each soil type. Moderate relationships have been found between Colwell K and wheat responses to K applications when similar soil types have been used (Wong et al. 2000). The relationship of critical values by the Colwell K method and yields of wheat, barley, canola, lupin, sunflower, sorghum and faba bean was studied, and it was reported that to achieve 90% relative yield, the critical value for each plant varied among soil types (Brennan and Bell 2013). Similarly inaccuracies have been found using the Colwell test

for P in predicting crop responses to P applications (Holford and Cullis 1985; Mason et al. 2010; Reuter et al. 1995).

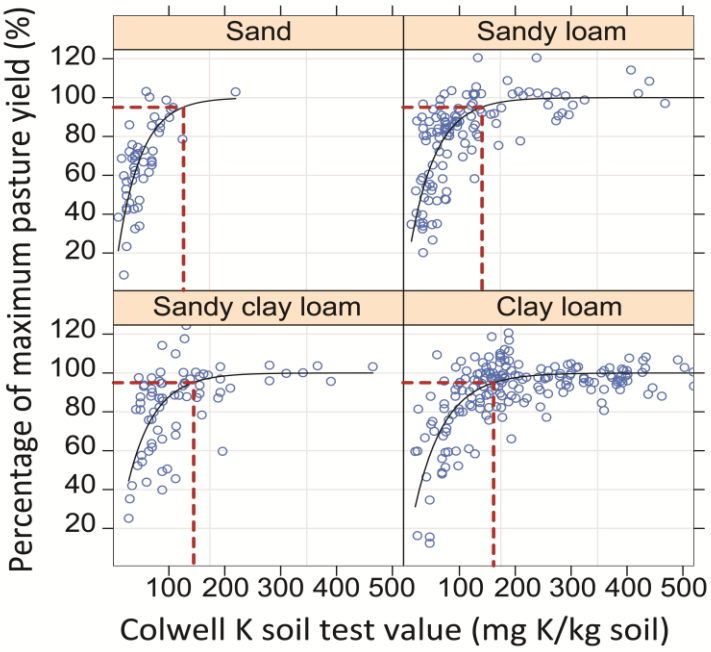


**Figure 1.7** The relationship between percentage of maximum pasture yield and Colwell K soil test values at 95% of pasture production are indicated by dashed lines (Gourley et al. 2007).

## 7. DGT technique

### 7.1. DGT introduction

DGT is a relatively new method for testing available elements in solution. The method has been mostly used to assay metal elements in water such as Cd, Cu, Fe, Mn, Ni and Zn (Dahlqvist et al. 2002; Davison and Zhang 1994; Schintu et al. 2010; Zhang and Davison 1995), and it has also been successfully used for Cd and Zn in sediments (Zhang et al. 1995). Greater accuracy was found for predicting plant-available P, for which the dominant uptake mechanism by plant roots is diffusion, using the DGT method compared to traditional extraction methods (Mason et al. 2013; Mason et al. 2010; Menzies et al. 2005; Six et al. 2012; Six et al. 2014; Speirs et al. 2013; Zhang et al. 1998a). The DGT device consists of two parts. The first part is a plastic piston and a plastic cap with a window of area A. The function of this part is to hold together tightly the gel assembly. The gel assembly contains

two polyacrylamide gels (diffusive gel and the binding layer) and an additional membrane filter acting as a protective barrier for the gels. A schematic of the device can be seen in Figure 1.8.

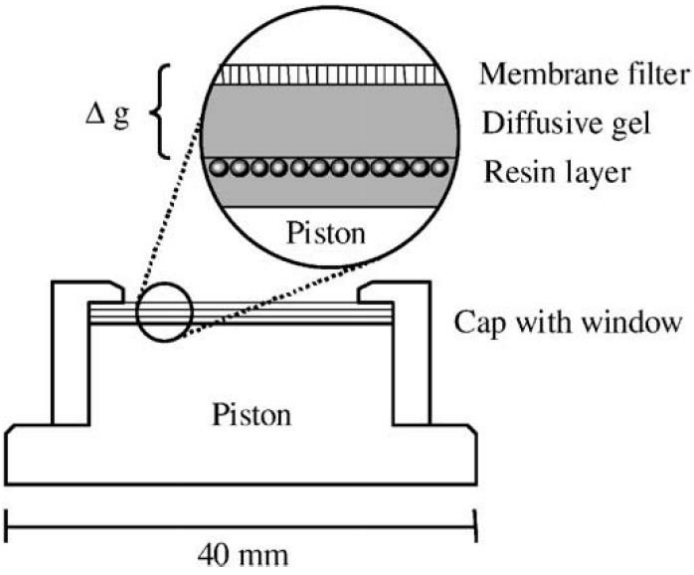


**Figure 1.8** Schematic representation of a cross section through the DGT device and hydrogel layers (Dahlqvist et al. 2002).

7.2. Process of DGT measurement on soils

When a DGT device is deployed on wet soil, with soil water content approximately equal to the water holding capacity (assessed visually), the elements in the soil solution pool diffuse through the diffusive gel and accumulate in the resin gel, and a gradient of concentration is quickly formed in the diffusive gel. The resin gel acts as an infinite sink for binding elements transported through the diffusive gel, thereby maintaining the diffusive gradient established in the diffusive gel. After a given deployment time, the binding gel is unloaded from the DGT device and rinsed with ultrapure water (18.2 MΩ cm). The elements absorbed are eluted in acid solution and the elements in the elution solution are then measured by a relevant procedure (Mason et al. 2005). The type of solution used is dependent on the analyte of interest. Finally the time-averaged element concentration measured by the DGT method, $C_{DGT}$, can be expressed as equation (1):

$C_{DGT}$=$M\Delta g/(\mathrm{DA}t)$(1)

where $M$ is the mass of K measured on the resin gel (mg), Δg is the total thickness of the diffusive gel and filter paper (cm); D is the diffusion coefficient of the target element in the diffusive layer at the temperature of deployment ($cm^2$ $s^{-1}$); A is the area of the exposure window ($cm^2$); and t is the deployment time (s).

7.3. The theory of the DGT method

The theory behind DGT methodology for assessment of available elements in soil environments has previously been described in more detail by Zhang et al. (1995), Mason et al. (2005) and Degryse et al. (2009). According to the element resupply ability from soil solid phases, there are three cases of element uptake by the DGT device (Figure 1.9): Case I - high resupply ability from soil phase - the flux remains the same throughout deployment time as the removal of element on the DGT surface is rapidly replenished from the soil solid phase; Case II - low resupply ability from soil phase - the flux decreases with deployment time due to poor resupply ability from soil phase; Case III - moderate resupply ability - a decreased but relatively consistent flux occurs due to moderate element resupply ability from the soil phase. Consequently, the time averaged $C_{DGT}$ reflects both the initial intensity of an element in soil solution and the resupply ability of the element with time.

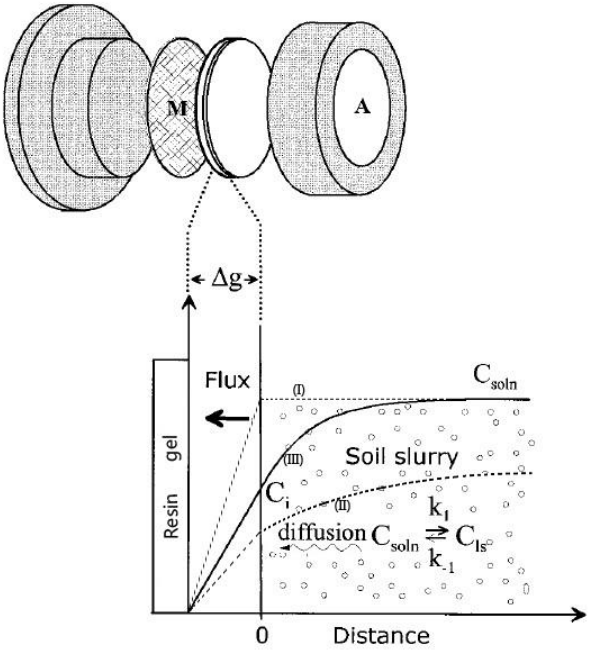


**Figure 1.9** Element uptake by DGTs modified from Ernstberger et al. (2002) and Zhang et al. (1998b).

7.4. Potential advantages of the DGT technique for K

Proposed advantages of the DGT technique over traditional extraction methods are that the technique mimics the processes by which K is accumulated by plants from soils, based on a diffusive theory as illustrated above. The biggest difference between DGT and traditional methods is that there are no additional chemicals added to the soil, although water is added to the soil samples during the deployment process. Thus, the natural equilibrium between the different pools of elements in the soil is not disrupted. Furthermore, the soil to water ratio used during DGT deployment (100 % WHC) is close to that in the field, unlike the wide soil: extractant ratios used by traditional K soil test methods. Hence, the concentrations of all ions in soil solution are quite similar to field conditions. In addition, significant shifts in soil pH are avoided in the DGT extraction process compared to that in a traditional chemical extraction method. Provided that DGT provides a useful predictor of plant-available K, there is great potential to better manage K fertilizer inputs, in addition to maximising yields and maximising profits for growers.

7.5. DGT methods of soil analysis

For different element assessments, the binding agents vary accordingly in order to match different binding abilities for each specific element. So far, many different materials have been incorporated into the gel for element absorption. For P, ferrihydrite and titanium dioxide were used to bind P in a DGT technique (Mason et al. 2008; Mason et al. 2010; Panther et al. 2010; 2011). Chelex-100 has been used to measure Ca, Cu, Pb and Zn (Nolan et al. 2005). The DGT method has initially been used to measure plant available K by Tandy et al. (2011; Tandy et al. 2012), using Amberlite IRP-69 as the resin gel. They proposed that a similar accuracy to the $NH_4OAc$ K method was observed when the DGT method was used to predict K concentrations of winter barley. However, limitations were also reported in terms of limited deployment time, lower concentration range and potential cation competition from Ca.

## 8. Conclusions and project aim

The DGT method has been proven to be an effective prediction method for trace metal availability in soils. It has also been reported to be capable of providing better accuracy than traditional extraction method for plant available P measurement. Compared to traditional extraction methods for assessment of available K in soil, DGT uptake and deployment conditions are more close to those under which plant K uptake occurs in the field. As the theory of the DGT method is based on element diffusion, which is the main mechanism of K uptake by plant roots, it is prudent to explore the applicability of the DGT method for measurement of plant available K in soils.

The aims of the following work are to focus on refinement and improvement of the DGT method for soil K measurement and assess the accuracy of the DGT K method to predict response of wheat to K fertilizer, compared with the traditional extraction methods for K.

Further investigation of the effects of potential competing cations on K uptake by the DGT method will be undertaken, as other cations present in soil solution are likely to be taken up by the resin gel used for K binding. Finally the accuracy of the DGT K method will be compared to the traditional extraction methods in relation to predicting plant response and uptake to application of K in the glasshouse using a wide range of soil types.

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# CHAPTER 2

## Optimization of the diffusive gradients in thin films (DGT) method for simultaneous assay of potassium and plant-available phosphorus in soils

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# Optimization of the diffusive gradients in thin films (DGT) method for simultaneous assay of potassium and plant-available phosphorus in soils

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ABSTRACT

Potassium (K) and phosphorus (P) are two important macronutrients for crops, and are usually applied to soils as granular fertilizer before seeding. Therefore, accurate soil tests prior to planting to predict crop response to fertilizers are important in optimizing crop yields. Traditional methods used for testing both available K and P in soils, which are based on chemical extraction procedures, are to be soil-type dependent, and the predictive relationships across a broad range of soils are generally poor. The diffusive gradients in thin films (DGT) technique, based on diffusion theory, is extensively used to measure the diffusive supply of trace elements, metals and some nutrients in soils and water. When DGT is used to assess plant-available P in soils, a good relationship is found between crop response to P fertilizer and concentrations of P in soil measured by DGT, and therefore the DGT method provides a more precise recommendation of P fertilizer requirements. Adaptation of the DGT method to measure plant-available K in soils has already been attempted [1], but limitations were reported due to the non-uniform size of the resin gel, decreased K binding rate of the gel at long deployment times and a limited ability to measure a wide range of K concentrations. To eliminate these problems, a new resin gel has been developed by combining Amberlite and ferrihydrite. This mixed Amberlite and ferrihydrite (MAF) gel has improved properties in terms of handling and even distribution of Amberlite in the gel. The elution efficiencies of the MAF gel for K and P were 90% and 96%, respectively. The diffusion coefficient of K through the diffusive gel was $1.30 \times 10^{-5}$ cm$^2$ s$^{-1}$ at $22 \pm 1$ °C and was stable through time. Since ferrihydrite is already used in DGT P testing, the ability of the MAF gel to assess available P simultaneously was also assessed. The MAF gel performed the same as the traditional ferrihydrite gel for available P assessment in a wide variety of agricultural soils. This means that the newly developed gel has the potential to measure K and plant-available P in soils simultaneously.



## 1. Introduction

Potassium (K) is one of the most important macronutrients in terms of accumulation by plants [2] and was defined as "the forgotten element" as early as 1997 [3]. Deficiency of K in soils has become a worldwide problem [4,5], especially in areas with coarse sandy soils or soils with high organic matter contents [6], which are often associated with low mineral K content [7]. Recently, there has been an increase in reported occurrences of K deficiency for wheat and canola crops grown in south western Australia [8]. Further, Rengel and Damon [9] report that 75% of the paddy soils in China and 67% of the wheat belt in southern Australia are deficient in K. Accurate determination of available K in soils through soil testing is essential for limiting yield losses associated with K deficiency [10] and maximising K fertilizer efficiency.

Scientists have long been seeking a method of testing plant-available K in soils that both has a good relationship to crop responses and suits a variety of soil types. Many different chemical extractants are used in traditional testing methods to extract certain parts of the K pool in soils, often with different concentrations and equilibration periods. In practical terms, the inaccuracy of these traditional soil tests was exemplified in a study by Gourley et al. [11]. Values of Colwell K (extracted by $NaHCO_3$) were classified according to different soil types, namely sandy soils, sandy loams, sandy clay loams and clay loams, and each was related to pasture response to K application. This process produced different critical soil testing values (soil K value at 95% of maximum relative yield) for each soil type. In addition, there was also a range of soil testing values having large variability around the critical value. Moderate relationships have been found between Colwell K and wheat responses to K applications when similar soil types were used

*Abbreviations:* DGT, diffusive gradients in thin films; MAF, mixed Amberlite and ferrihydrite gel; MDL, minimum detection limit.

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[12]. Therefore, the accuracy of current traditional soil testing methods for K appears to be soil type/region dependent, and the traditional soil testing method generally fails to provide an accurate indication of how much K fertilizer should be applied before planting.

Phosphorus (P) is another important macronutrient required in large amounts by plants. It is reported low initial P fertilizer utilization efficiency (5–25%) by crops has been attributed to the high P immobilisation capacity of soils in many cropping areas in Australia, especially those with alkaline soils [13,14]. Foliar application of P to correct P deficiency is only adoptable in soils with low P status [15,16]. Therefore, it is important to measure the plant-available P status in soil through soil testing before seeding, to promote efficient use of P fertilizer. However, the traditional extraction methods used for available P estimation also measure in some cases non-labile and stable forms of P [13,17,18]. Therefore, the accuracy of the extraction methods for P testing also needs to be improved.

Most of the K and P available for plant uptake move to the plant root surface by diffusion. The initial uptake of K and P by plant roots lowers the concentrations at the root surface, therefore a concentration gradient is established and diffusion is promoted [19]. The Diffusive Gradients in Thin-films (DGT) technique is also based on diffusion theory and the DGT device acts similarly to plant roots with regard to uptake of an element. When the DGT device is deployed on wet soil, the inner resin gel absorbs the diffusive element establishing a concentration gradient which effectively lowers the concentration of the element at the DGT/soil interface, promoting further diffusion of the element from the soil solution phase. Because of the similarity between P uptake by plant roots and the accumulation of P by the DGT device, the P pools measured by the DGT technique are more closely related to plant-available P [18] and to growth responses from addition of P fertiliser compared to those of the traditional chemical extraction methods [20–23].

In contrast to the traditional chemical methods, the DGT technique measures the analyte in both soil solution and that resupplied from the solid phase in sediments or soils. The DGT technique has been successfully used to assay metal elements with greater accuracy than chemical extraction methods: Cd, Cu, Fe, Hg, Mn, Ni, Zn, etc. in water [24–28]; Cd, Cu, Fe, Mn, Ni and Zn in sediments [29]; and Cd, Cu, Pb and Zn in soils [30–32]. Recently, Tandy et al. [1] developed the DGT technique for determination of plant-available K in soils using Amberlite IRP-69 as the resin gel. This reagent had a capacity of 880 μg K per device, which was large enough for K testing in soils. However, the resin gel was non-uniform in size and generated different diffusive path lengths for K, thereby lowering the accumulation rate of K on the resin gel after a certain amount of K was accumulated, even though the gel capacity had not yet been reached.

The aim of the present research was to improve the resin gel for K testing in soils using the DGT technique, including testing different gel configurations and the diffusion coefficient of the diffusive gel for K. The ability of the mixed Amberlite and ferrihydrite (MAF) gel, which was selected for further testing on the basis of its even distribution of Amberlite reagent and flat contact surface, in measuring plant-available P was assessed as well, to investigate the possibility of developing the DGT method for simultaneously testing of K and plant-available P.

## 2. Material and methods

### 2.1. Binding gel optimization for K measurement using DGT

#### 2.1.1. Potassium binding gels and DGT device preparation

Plastic DGT devices (DGT Research Ltd, Lancaster, UK) with an effective sampling area of 2.54 $cm^2$ were used to load the gel assemblies containing resin gel, diffusive gel and filter paper. The diffusive gels were prepared and cast according to published procedures with a thickness of 0.6 mm [27,33], and the Glass Fiber Filter paper (0.45 μm, Toyo Roshi Kaisha, Ltd., Japan) were 0.2 mm thick.

Amberlite (IRP-69 ion-exchange resin, 100–500 wet mesh) was used as a binding reagent in the resin gel due to its previously identified ability to bind K in sufficient amounts [1]. To obtain a binding layer with the reagent evenly distributed, two procedures were tested: (1) Amberlite was ground into small particles using a mortar; and (2) Amberlite was mixed with ferrihydrite, a reagent previously used for DGT P testing in soils [33]. In order to accommodate the increase in the total amounts of Amberlite and ferrihydrite in the binding gel, amounts of ammonium persulfate and TEMED (*N*,*N*,*N*',*N*'-Tetramethylethylenediamine) were also increased in every 5 mL gel solution. Four gel configurations containing Amberlite and/or ferrihydrite were tested in this study, Amberlite gel (A), Ground Amberlite gel (GA), ground Amberlite and ferrihydrite gel (GAF) and mixed Amberlite and ferrihydrite gel (MAF). Details of the gels and reagent amounts used are presented in Table 1. The casting process was as described by Zhang [27].

#### 2.1.2. DGT blanks and minimum detection limits

The minimum detection limits (MDL) were calculated according to the Analytical Method Committee procedures [34], equalling the average of the blank values plus three times the standard deviation. The detection limits obtained were based on an equivalent 24 h deployment period of the DGT devices, and two to four blanks of the four gels were tested.

#### 2.1.3. Elution and uptake efficiencies of binding gels

For gels A, GA and GAF, initially 1 mL of K solution (as KCl), containing 0, 10, 20, 30 and 40 mg $L^{-1}$ K, were used to test elution and uptake efficiencies. Solutions were placed on an end-over-end shaker for 24 h. Gels were then transferred to 1 mL of 1 mol $L^{-1}$ HCl solution for elution and 9 mL of Milli-Q water was used for dilution before analysis. Potassium concentrations in solution and eluent were measured by inductively coupled plasma-optical emission spectrometer (ICP-OES, PerkinElmer, Optima 7000DV) at $\lambda$=766.490 nm. For the MAF gel, the elution efficiency was tested separately in 10 mL solutions containing 0, 5, 10, 20 and 30 mg $L^{-1}$ K (as KCl). For all the above elution and uptake efficiency tests, three replicates were used for each treatment. Elution efficiency ($f_e$, Eq. (1)) and uptake efficiency ($f_u$, Eq. (2)) can both be calculated by measuring original and final concentrations of K solutions after exposure to binding gels as follows:

$$f_e = \frac{c_{Acid} \times 10.265}{M_{Initial} - M_{Final}} \times 100 \quad (1)$$

$$f_u = \frac{M_{Initial} - M_{Final}}{M_{Initial}} \times 100 \quad (2)$$

where $c_{Acid}$ is the K concentration in HCl solution after the K was eluted (mg $L^{-1}$); "10.265" is the dilution factor (mL), equals to the

**Table 1**
Composition of binding gels.

| Gel | Reagent for 5 mL gel solution (in wet weight) | Ammonium persulphate (μL) | TEMED (μL)[a] |
|---|---|---|---|
| A | 2 g Amberlite | 25 | 10 |
| GA | 2 g ground Amberlite | 25 | 10 |
| GAF | 1 g ground Amberlite + 1 g ferrihydrite | 25 | 10 |
| MAF | 2 g Amberlite + 1 g ferrihydrite | 30 | 12 |

[a] TEMED refers the reagent *N*,*N*,*N*',*N*'-Tetramethylethylenediamine.

total volume of 1 mL of acid solution, 9 mL of Milli-Q water for dilution and 0.265 mL of the gel volume; and $M_{Initial}$ and $M_{Final}$ are the measured amounts of K in the solution before and after immersion of the binding gels (μg).

#### 2.1.4. Capacity assessment

Gels A, GA and GAF were used to investigate the effect of two procedures on K-binding capacity: (1) grinding the Amberlite resin; and (2) mixing ferrihydrite with Amberlite resin. Potassium solutions (3 L as KCl) with different concentrations were used to provide the gels with various amounts of K. The concentrations of K in solution were 20, 40, 60, 80, 100, 120, 140, 160, 180, 200, 220 and 240 mg $L^{-1}$. The solution was stirred vigorously and DGT devices were deployed for up to 24 h, with temperature recorded at regular intervals throughout the experiment (three replicates for each treatment). The amount of K accumulated by gels can be calculated by Eq. (3) as follows:

$$M = M_{Acid}/f_e \quad (3)$$

where $M_{Acid}$ is the mass of K measured in the retrieved acid solution. The capacity equals the mass of K on gel (M) at the concentration where relationship between K uptake by the gel and solution concentration becomes non-linear.

#### 2.1.5. Diffusion coefficient measurement

DGT devices accommodated by specialised plastic holders were deployed in two boxes of 3 L of 40 mg $L^{-1}$ K (as KCl) solution for between 1 and 24 h, containing nine devices in each box. For each deployment period, three DGT devices were removed from one of the boxes. The solution temperature was recorded at regular intervals. After each deployment period DGT devices were rinsed with Milli-Q water, and the MAF gel was retrieved and placed in 1 mL of 1 mol $L^{-1}$ HCl solution. The diffusion coefficient of K, D ($cm^2$ $s^{-1}$), was calculated using Eq. (4) [35]:

$$D = \frac{slope \times \Delta g}{A \times C_{solution} \times 60} \quad (4)$$

where "slope" is the measured K amount on gel with deployment time (ng $min^{-1}$); $\Delta g$ is the thickness of the diffusive gel (mm); $A$ is the effective area of the DGT device ($cm^2$); $C_{solution}$ is K concentration in solution (mg $L^{-1}$) and "60" converts the deployment time from minutes into seconds.

### 2.2. Comparison of the MAF gel with ferrihydrite-only gel for P testing

#### 2.2.1. DGT blanks and minimum detection limit

The minimum detection limit (MDL) for P was measured and calculated as described for K above. Five replicate MAF gels were used.

#### 2.2.2. Phosphorus elution and uptake efficiencies of the MAF gel

Phosphorus solutions (as $KH_2PO_4$, 10 mL) containing 0, 0.1, 0.2, 0.4 and 0.6 mg $L^{-1}$ P were used for assessment of P elution and uptake efficiencies, replicated three times. The procedures were as outlined above for K.

#### 2.2.3. Phosphorus uptake by the MAF and ferrihydrite gels

DGT devices containing either the MAF gel or ferrihydrite gel were deployed for eight different periods (1, 2, 4, 8, 12, 16, 20 and 24 h) in 4 L stirred solution containing 1.2 mg $L^{-1}$ P as $KH_2PO_4$. After the devices were dismantled the P on the binding gels was eluted using 1 mL of 1 mol $L^{-1}$ HCl. All treatments were replicated three times.

#### 2.2.4. Soil characterisation and DGT P measurement

Sixteen soils from agricultural regions in Australia (Table 2) were dried at 40 °C in the oven to constant weight and sieved to $<2$ mm. Phosphorus buffering index (PBI) was measured using the method described by Moody (2007) [36]. Soil pH was measured in 0.01 mol $L^{-1}$ $CaCl_2$ solution in a soil to solution ratio of 1:5 [37]. Total organic carbon was measured according to Rayment and Higginson [37]. Colwell K was extracted by 0.5 mol $L^{-1}$ $NaHCO_3$ [37]. Exchangeable K was extracted using 1 mol $L^{-1}$ $NH_4OAc$ [37]. Particle size was determined using the method described in McKenzie et al. (2002) [38].

The DGT devices were prepared as described above for K, containing either the MAF gel or ferrihydrite gel. Before deploy the DGT devices on the soils (approximately 50 g), they were wetted with Milli-Q water to saturation point (assessed visually) and left overnight in Petri dishes. DGT devices containing either the MAF gel or ferrihydrite only gel were deployed on the soils. After 24 h deployment, the devices were dismantled and the gels were placed into 1 mol $L^{-1}$ HCl. Three replicates were used for each treatment. Concentrations of P and K in eluent were measured by ICP-OES as outlined above, and $\lambda$ for P testing is 214.914 nm. Concentrations of P and K as determined using DGT

**Table 2**
Basic properties of the Australian agricultural soils used.

| Site | Abbreviation | State | PBI | pH | TOC (%) | Colwell K (mg $kg^{-1}$) | Exchangeable K (mg $kg^{-1}$) | Clay (%) | Silt (%) | Sand (%) | K measured on MAF gel (μg)[a] |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Langhorne Creek | LC | SA | 2 | 6.7 | 0.80 | 193 | 165 | 4.1 | 1.4 | 92 | 133 |
| Wharminda | WD | SA | 21 | 6.4 | 0.85 | 198 | 161 | 2.9 | 0.5 | 95 | 141 |
| Stansbury | SB | SA | 23 | 5.7 | 1.10 | 77 | 60 | 1.7 | 0.8 | 95 | 34 |
| Karoonda | KD | SA | 24 | 6.4 | 0.40 | 78 | 51 | 2.4 | 0.4 | 96 | 65 |
| Ngarkat | NK | SA | 25 | 6.6 | 0.67 | 67 | 29 | 2.1 | 1.1 | 95 | 23 |
| Mount Damper | MD | SA | 30 | 6.6 | 0.50 | 99 | 69 | 3.5 | 0.7 | 94 | 54 |
| Walpeup LTP | WL | VIC | 50 | 6.8 | 0.49 | 395 | 389 | 8.7 | 3.2 | 86 | 161 |
| Ilanson | IN | SA | 56 | 6.3 | 1.50 | 406 | 252 | 13.1 | 24.1 | 59 | 74 |
| Koppio | KP | SA | 58 | 6.8 | 3.93 | 396 | 282 | 14.7 | 10.7 | 67 | 150 |
| Boyup Brook | BB | WA | 79 | 5.8 | 3.00 | 28 | 18 | 3.8 | 2.5 | 87 | 14 |
| Condobolin | CN | NSW | 85 | 5.7 | 1.20 | 754 | 741 | 27.6 | 12.1 | 57 | 241 |
| Lochearn | LN | NSW | 99 | 7.0 | 0.70 | 706 | 744 | 35.4 | 25.6 | 35 | 55 |
| Birchip | BC | VIC | 108 | 7.1 | 0.72 | 571 | 673 | 43.0 | 8.5 | 43 | 27 |
| Mudamuckla | MK | SA | 127 | 7.6 | 0.70 | 411 | 415 | 7.7 | 2.4 | 62 | 134 |
| Kelly | KY | NSW | 175 | 7.3 | 1.10 | 617 | 775 | 52.3 | 23.5 | 17 | 32 |
| Pt.Kenny | PK | SA | 183 | 7.5 | 2.94 | 433 | 451 | 9.9 | 3.7 | 24 | 94 |

[a] Required 24 h deployment of the DGT devices containing the mixed Amberlite and ferrihydrite (MAF) gel using 0.6 mm diffusive gel plus 0.2 mm filter paper.

were calculated by Eq. (5):

$$C_{DGT} = M\Delta g/DAt \quad (5)$$

where $C_{DGT}$ is the concentration of element measured by DGT ($\mu g\ L^{-1}$); $M$ is measured amount of P or K on gel; $t$ is the deployment time (s).

## 3. Results and discussion

### 3.1. DGT improvement for K testing

#### 3.1.1. DGT blanks and MDL

The minimum detection limits (MDL) of the gels employed for K binding are presented in Table 3. The standard error of the blanks for each gel was much smaller than the averaged K amount on each gel, suggesting the number of blanks did not affect the MDL. The mass of K on the MAF gel was 7.9 μg, greater than the previously reported 1.4 μg [1]. The MDL of DGT K using 0.6 mm diffusive layer was 298 $\mu g\ L^{-1}$ ($C_{DGT}$). However, the minimum amount of K accumulated by gels from the 16 soil samples was 14 μg (Table 2), equivalent to a $C_{DGT}$ of 511 $\mu g\ L^{-1}$ at 24 h deployment. Therefore, a MDL of 298 $\mu g\ L^{-1}$ was reasonable for DGT K testing in agricultural soils. Compared with the MDL of the MAF gel, the MDLs of gels A, GA and GAF were much higher (Table 3). These three gels are unsuitable for use in DGT devices to measure K in soil. Sufficient amount of blanks can provide an accurate K background value and MDL, so that errors can be eliminated by deducting it from samples measured.

#### 3.1.2. Elution and uptake efficiencies

The elution efficiencies averaged 88%, 88%, 96% and 90% for gels A, GA, GAF and MAF respectively, with no significant difference between gels ($P \leq 0.05$, Table 4). The elution efficiency of 90% for the MAF gel was close to the previously reported value (91%) for Amberlite gel [1]. It can therefore be concluded that neither grinding Amberlite nor adding ferrihydrite affects the elution efficiency of Amberlite-based gels for K.

**Table 3**
Calculated blank (mean and standard deviation) and method detection limit (MDL) for K using different gels.

| Gel | Blank μg device$^{-1}$ | MDL μg device$^{-1}$ | MDL[a] μg $L^{-1}$ | N |
|---|---|---|---|---|
| A | 16 ± 0.19 | 19.5 | 713 | 3 |
| GA | 14 ± 0.03 | 13.9 | 507 | 3 |
| GAF | 9 ± 0.02 | 15.2 | 557 | 2 |
| MAF | 7.9 ± 0.03 | 8.2 | 298 | 4 |

[a] Required solution concentration to obtain MDL for a 24 h deployment using a 0.6 mm diffusive gel plus 0.2 mm filter paper; $N$ represents the number of replicates.

**Table 4**
Mean and standard deviations (SD) for elution efficiencies ($f_e$) and uptake efficiencies ($f_u$) of gels for K.

| Gel | $f_e$ | | $f_u$ | |
|---|---|---|---|---|
| | Mean (%) | SD | Mean (%) | SD |
| A | 88a | 3.95 | 99a | 0.25 |
| GA | 88a | 4.00 | 99a | 0.13 |
| GAF | 96a | 5.56 | 99a | 0.16 |
| MAF | 90a | 1.78 | 96b | 0.34 |

Values in a column with the same letters are not significantly different ($P \leq 0.05$, $n=3$).

The uptake efficiency of each gel for K was very consistent between replicates at each concentration, averaging 99% for gels A, GA and GAF and 96% for Gel MAF. Significant differences ($P \leq 0.05$) between these uptake efficiencies suggested that the presence of ferrihydrite lowered K uptake only with the MAF gel (Table 4). This was possibly due to the slightly different experimental method used. Similar uptake efficiencies between gels GAF, A and GA suggest that neither the inclusion of ferrihydrite nor grinding the Amberlite affects the utilization ability of the DGT in K testing.

#### 3.1.3. Capacity assessment and gel selection for subsequent testing

The effects of grinding Amberlite and mixing with ferrihydrite on capacities for K were assessed in the K uptake experiment. A linear relationship between K uptake and K solution concentration was only found for the lowest two K concentrations (Fig. 1). The capacities of gels A and GA were similar, ranging from approximately 756 to 985 μg for Gel A and from 815 to 940 μg for Gel GA, which was consistent with those previously reported [1]. Therefore, the capacity of the binding gel was not increased by grinding the Amberlite. The capacity of Gel GAF was above 425 μg, roughly half the capacities of gels A and GA. It can be concluded that the capacity of Gel GAF was reduced mainly due to the lower amount of Amberlite in the gel (Table 1). Nevertheless, ferrihydrite does not reduce the capacity of Amberlite per gram for K. The maximum amount of K accumulated on the gel after 24 h deployment for 16 different Australian agricultural soils was 241 μg (Table 2), which was far less than the capacity obtained for all the gels used. Thus, the capacity of all the gels employed appears large enough for the assessment of K in agricultural soils in Australia.

Whilst a binding gel with high K capacity is very important for K testing by the DGT method, in terms of physical features, a well-built, strong and flat-surface gel with the reagent evenly distributed is ideal. Grinding Amberlite made no difference to the gel shape, as gels A and GA curled in a similar way, presumably because the Amberlite settles due to gravity more on one side of the plate during gel polymerisation. The non-evenly distributed Amberlite in gels A and GA resulted in different proportions of gel solution appearing on the top side of the set gel than on the underside. This caused differential expansion on the top and bottom of the gel when the gel was hydrated in water, leading to curling. Additional attempt of using increased amount of ammonium persulfate and TEMED in Gel A also failed in improvement of Amberlite distribution in the gel assessed visually by its curling shape. However, with the presence of ferrihydrite in the gels GAF and MAF, both gels GAF and MAF were completely flat and the Amberlite was more evenly distributed in the resin gels. This also made the process of preparing the DGT devices much easier for potential commercial laboratory use. Gel GAF was flatter than gels A and GA, because ferrihydrite slowed the settling of Amberlite so that it was more evenly distributed in the gel at the end of polymerisation.

Amberlite settles due to gravity not only more on one side of the plate during gel polymerisation, but also more at the bottom part of the plate, resulting in different amount of Amberlite contained in each gel after the gel sheet is cut to required shape. Therefore, the errors in the K uptake experiment (Fig. 1) are more likely to reflect K uptake difference by gels more than systematic error between the three replicates during the test, reflecting the total amount of Amberlite distributed in each gel. The errors for Gel GA in the capacity test was smaller than that for Gel A, presumably because the amounts of Amberlite present in each gel were more consistent in the replicates of Gel GA due to the similar size distribution compared to those of Gel A. The errors for Gel GAF were also smaller than that for gels A and GA. Therefore, the

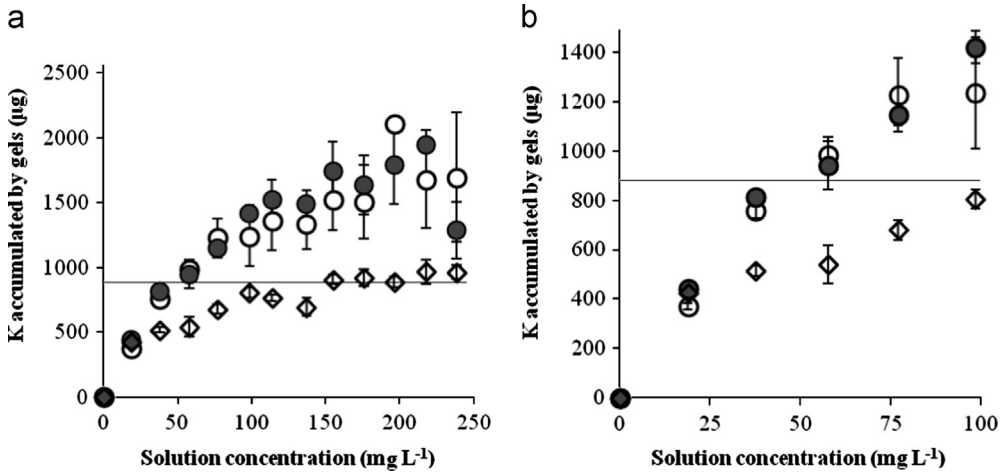


**Fig. 1.** Accumulation of K by 3 different gels (○ Gel A, ● Gel GA, ◇ Gel GAF) after 24 h in solution differing in K concentration. ((a) all solutions and, (b) solutions with low K concentrations; the horizontal solid line indicates the capacity of 880 μg reported by Tandy et al. [1]). Error bars represent standard errors from three replicates.

presence of ferrihydrite assists in generating an even spatial, and hence quantitative, distribution of Amberlite in the binding gel.

In conclusion, the capacity of the Amberlite-based binding gel is reduced simply due to dilution, but it is still sufficient for K binding in agricultural soils. In addition, improved gel properties in terms of shape and Amberlite reagent distribution are also observed in the MAF gel. Therefore, the MAF gel was selected for use in subsequent experiments.

### 3.1.4. Capacity assessment of the MAF gel for K and diffusion coefficient measurement

The amount of K accumulated by the MAF gels increased linearly with time until 8 h in 40 mg $L^{-1}$ K solution (Fig. 2), which was an improvement to the utilization limits described by Tandy et al. [1], namely, that the deployment time should be shorter than 2 h and K concentration should be less than 16 mg $L^{-1}$. The decreased slope of K uptake by the DGT device with time after 8 h indicates K concentration at the resin gel surface is not zero. Presumably because the binding sites of Amberlite on top part of the resin gel are saturated, reaching a practical capacity, 450 as indicated. After 8 h deployment, a significantly decreased K binding rate appears due to further diffusion of K into resin gel and more K can be accumulated until the theoretical capacity is reached which is associated with the amount of Amberlite contained in the gel. A linear uptake of K with deployment time up until 24 h was also observed in lower K concentration solution (15 mg $L^{-1}$ K solution) was reached (data not shown). In comparison of the maximum K amount of 241 μg accumulated in agricultural soils in Australia, the practical capacity of 450 μg is sufficient for DGT K testing using the MAF gel, at least larger than the practical capacity of the Amberlite gel in Tandy et al.'s work, not the theoretical capacity of 880 μg as suggested.

The diffusion coefficient was calculated according to the slope of K uptake and deployment time within 8 h (linear part, $R^2=1.00$). A diffusion coefficient of $1.30\times10^{-5}$ $cm^2$ $s^{-1}$ at $22\pm1$ °C was obtained and was only 72% of the value in water ($1.81\times10^{-5}$ $cm^2$ $s^{-1}$) [39], which Tandy et al. used previously. The reason for the difference is presumably that K accumulated further in the MAF gel with the addition of ferrihydrite rather than on the surface of the Amberlite gel Tandy et al. used when the DGT devices are deployed in solution. Therefore, an extra-unknown diffusion distance of K diffusion through the resin gel might be contributable to the decreased diffusion coefficient compared with Tandy et al.'s. Since we used a binding gel with better reagent distribution and a larger practical capacity, K in soils can therefore

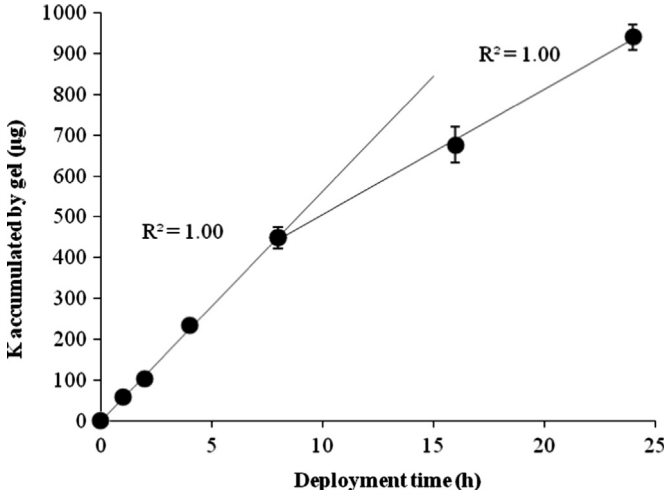


**Fig. 2.** Accumulation of K by the MAF gel during different deployment periods in 40 mg $L^{-1}$ K solution. Error bars represent standard errors from three replicates.

be measured using the MAF gel for a wider range of K concentrations in soils and with longer deployment periods if necessary, which increases the utility of the technique.

## 3.2. Application of the MAF gel for P testing

### 3.2.1. DGT blanks and MDL of the MAF gel for P

The amount of P in blanks ($n=5$) averaged 91 ng on the MAF gel, greater than the 28 ng previously reported by Mason et al. (2005) [33] using ferrihydrite gel. Compared with the MDL of 4.8 μg $L^{-1}$ reported by Mason, the MDL for the MAF gel was 10.1 μg $L^{-1}$. These differences may be attributable to minor P contamination in the Amberlite, or the higher detection limit of ICP-OES compared to inductively coupled plasma mass spectrometry (ICP-MS) used by Mason et al. [33]. The equivalent critical DGT P ($C_{DGT}$) from a large series of field trials in southern Australia was identified to be around 66 μg $L^{-1}$ for wheat at maturity in field [21], which was also greater than the MDL of the MAF gel for P. Thus, the MDL of the MAF gel for P testing using DGT is likely not a problem.

### 3.2.2. Elution and uptake efficiencies of the MAF gel

The efficiency of P elution from the MAF gel averaged 96% (Table 5), similar to the ferrihydrite gel [33]. The P uptake efficiency

**Table 5**
Mean and standard deviation (SD) for elution efficiency ($f_e$) and uptake efficiency ($f_u$) of the mixed Amberlite and ferrihydrite (MAF) gel for P.

| P concentration (mg $L^{-1}$) | $f_e$ | | $f_u$ | |
|---|---|---|---|---|
| | Mean (%) | SD | Mean (%) | SD |
| 0.1 | 98a | 5.0 | 100a | 0 |
| 0.2 | 92a | 2.4 | 100a | 0 |
| 0.4 | 99a | 8.2 | 98a | 1.7 |
| 0.6 | 95a | 2.5 | 100a | 0 |
| **Mean** | **96** | **4.5** | **99** | **0.4** |

Values in a column with the same letters are not significantly different ($P \leq 0.05$, $n=3$).

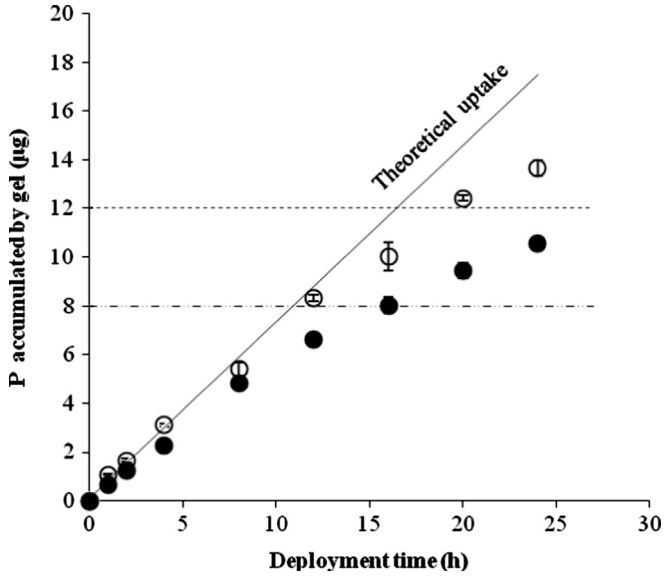


**Fig. 3.** Accumulation of P from solution (1.2 mg $L^{-1}$ P) by both the MAF gel (●) and ferrihydrite gel (○) at different deployment periods (– – – – indicates the capacity of ferrihydrite gel reported by Mason et al. [33] and — · · — indicates the theoretical capacity of the MAF gel calculated according to the amount of ferrihydrite contained in the gel). Error bars represent standard errors from three replicates.

of the MAF gel averaged 99%. Hence, the presence of Amberlite in the MAF gel does not appear to affect P uptake by the ferrihydrite.

### 3.2.3. Phosphorus uptake by the MAF gel and ferrihydrite gel

The accumulated P increased linearly and similarly on both the MAF and traditional ferrihydrite gels in 1.2 mg $L^{-1}$ P solution until 8 h deployment (Fig. 3). However, after 8 h deployment, differences became apparent in P uptake by the MAF and the ferrihydrite gels, likely due to the different amounts of ferrihydrite contained in the gels, thereby resulting in different P capacities of the two gels. Likewise, it can be concluded that the presence of Amberlite does not hinder the uptake of P by ferrihydrite in the MAF gel although capacity is reduced due to less ferrihydrite being contained in the gel. Compared to the theoretical P uptake, the slightly lowered P uptake rate by the MAF gel may be due to the diffusive pathway is potentially slightly longer for P to contact ferrihydrite when close to capacity for the MAF with inclusion of Amberlite. As long as the gel has not reached its capacity for P, both the MAF gel and ferrihydrite gel perform similarly.

### 3.2.4. DGT P soil testing using the MAF and ferrihydrite gels

To assess the effects of the increased P detection limit and reduced P capacity of the MAF gel based on the current ferrihydrite

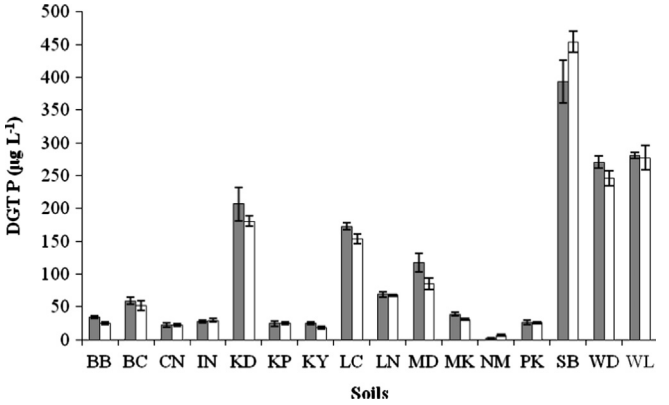


**Fig. 4.** Concentrations of P accumulated by DGT (expressed as $C_{DGT}$) in a variety of soils obtained using the MAF gel (■) and ferrihydrite gel (□), LSD = 7.42 μg $L^{-1}$ at level $P \leq 0.05$. Error bars represent standard errors from three replicates.

amount employed (Table 1), DGT devices containing either the MAF gel or the ferrihydrite gel were deployed on 16 agricultural soils from Australia, including samples with both high and low P concentrations. There was no significant difference ($P \leq 0.05$) between the results obtained using the MAF gel and the traditional ferrihydrite gel for plant-available P testing using the DGT technique where all the locations were tested together (Fig. 4). After testing them separately using the T test, significantly higher DGT P values were obtained using the MAF gel for BB, KY and MK while for NM the ferrihydrite gel had a significantly higher DGT P value compared to MAF. However, this soil had DGT P values very close to the MDL for P. Therefore, any difference in the DGT P measurement was not due to any effect of Amberlite on the ability of ferrihydrite to bind P but perhaps due to an experimental artefact that we cannot explain. Soils where a significant difference occurred all had very low DGT P readings, which could allude to varying background contributions of the MAF. Therefore, the MAF gel is an ideal alternative for ferrihydrite gel in DGT P testing, as the MAF gel can potentially measure K and plant-available P in soils simultaneously.

## 4. Conclusions

A resin gel for assessing concentrations of K in soils using the DGT technique was optimized by combining Amberlite and ferrihydrite. Compared with the K binding resin gel reported previously [1], the newly developed gel has an even distribution of the Amberlite resin used for binding K. As a consequence, the gel sets in a flat shape, which makes the procedure of loading the gel assemblies on DGT devices significantly easier. Furthermore, because the reagent was evenly distributed in the resin gel, it was possible to avoid the problem of poor K uptake rate associated deployment time limitation, which were assumed to be due to the non-homogeneous resin gel described previously by Tandy et al. [1]. Using the improved K binding gel, the diffusion coefficient was re-tested and a stable diffusion coefficient value of $1.30 \times 10^{-5}$ $cm^2$ $s^{-1}$ was obtained for K at $22 \pm 1$ °C. Importantly, potential impacts of competing cations in soils on K measurement using DGT needs to be assessed with the new MAF gel before it can be fully utilised in agricultural soils.

The presence of Amberlite resin in the gel did not hinder the binding ability of ferrihydrite for P, and the capacity of the MAF gel was still satisfactory for P testing in agricultural soils. The traditional ferrihydrite gel can thus be substituted by the MAF gel. With the same ability for P testing using the DGT technique, the newly developed MAF gel provides the possibility of simultaneous assessment of DGT K and DGT P in soils.

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# CHAPTER 3

## Application of the diffusive gradients in thin films technique for potassium measurement in agricultural soils: Effects of competing cations on potassium uptake by the resin gel

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## Author Contributions

By signing the Statement of Authorship, each author certifies that their stated contribution to the publication is accurate and that permission is granted for the publication to be included in the candidate's thesis.

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| Contribution to the Paper | Experimental development, performed analysis on all samples, data analysis and critical interpretation, wrote the manuscript. | | |
| Signature | | Date | |

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# Application of the diffusive gradients in thin films technique for available potassium measurement in agricultural soils: Effects of competing cations on potassium uptake by the resin gel

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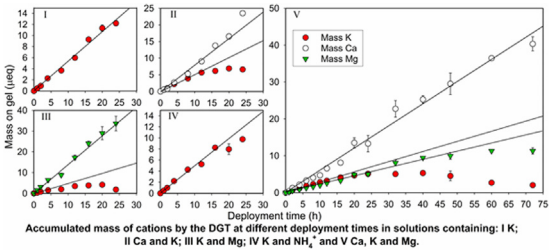
## HIGHLIGHTS

- K uptake by DGT was investigated in the presence of competing cations in solution.
- Main cations had no effect on K elution/uptake efficiencies under capacity limit.
- A lower K diffusion coefficient was found in the presence of competing cations.
- DGT measured a different K pool compared to standard extraction methods.
- The mixed Amberlite and ferrihydrite gel had the ability to measure Ca and Mg.

## GRAPHICAL ABSTRACT




Accumulated mass of cations by the DGT at different deployment times in solutions containing: I K; II Ca and K; III K and Mg; IV K and $NH_4^+$ and V Ca, K and Mg.

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## ABSTRACT

The utilization of Amberlite (IRP-69 ion-exchange resin, 100–500 wet mesh) as the binding phase in the diffusive gradients in thin films (DGT) technique has shown potential to improve the assessment of plant-available K in soils. The binding phase has recently been optimized by using a mixed Amberlite and ferrihydrite (MAF) gel which results in linear K uptake over extended deployment periods and in solutions with higher K concentrations. As restriction of K uptake by Ca on the Amberlite based resin gel has been previously proposed, potential competing effects of $Ca^{2+}$, $Mg^{2+}$ and $NH_4^+$ on K uptake by the MAF gel were investigated. These cations had no effect on K elution efficiency which was 85%. However, K uptake by the MAF gel was restricted in the presence of competing cations in solution. Consequently, the diffusion coefficient of K decreased in the presence of cations compared to previous studies but was stable at $1.12 \times 10^{-5}$ $cm^2$ $s^{-1}$ at 25 °C regardless of cation concentrations. Uptake of K by the DGT device was affected by the presence of excessive Ca in more than 30% of twenty typical Australian agricultural soils. However, this problem could be circumvented by using a shorter deployment time than the normal 24 h. Moderate correlation of concentrations of K extracted by DGT with Colwell K (extracted by $NaHCO_3$, $R^2 = 0.69$) and $NH_4OAc$ K ($R^2 = 0.61$) indicates that DGT measures a different pool of K in soils than that measured by the standard extractants used. In addition, the MAF gel has the ability to measure Ca and Mg simultaneously.


*Abbreviations:* DGT, diffusive gradients in thin films; MAF, mixed Amberlite and ferrihydrite gel.

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## 1. Introduction

Potassium (K) is an important element required for plant growth, as it plays a significant role in many plant mechanisms, such as controlling cell extension and osmoregulation, enhancing enzyme activation and improving protein synthesis [1–3]. Potassium deficiency can lead to reduced value or quality in crop products, for example a decreased wheat seed size or an increased bitterness in lupins due to accumulation of alkaloids [4]. Glasshouse studies have shown that K deficiency in cotton can result in smaller organs at sites typically away from the main stem source leaves [5]. A higher population of soybean aphid is also attributed to K deficiency in the Midwest United States [6]. It is generally accepted that a sufficient K status reduces the incidence rate of plant diseases and pests [7–9]. Grewal [10] reported sufficient K could increase the frost resistance of potato. In adequately supplied plants, K may account for up to 6% of the total dry matter [11].

Potassium uptake by plants is affected not only by the amount of available K in soils, but also by the presence of other cations prevalent in soils. The most abundant cations in soils are calcium ($Ca^{2+}$), magnesium ($Mg^{2+}$), $K^+$, sodium ($Na^+$), and aluminium ($Al^{3+}$) common in acidic soils [12]. Some cations are dissolved in soil solution while others are held by the soil solid phase, and these two pools are often in equilibrium with each other. The quantity–intensity (Q/I) relationship is used to express available K in the presence of competing cations in soils [13,14], where the available K for plants in soils is dependent on both the solution K and the ratio of K to Ca and Mg. Due to the different chemical properties of, and selectivity for, the cations in soil solution by plants, the availability/accessibility of any cation can be affected by others. Evidence regarding these effects is inconsistent. For example, York et al. [15] concluded that Ca did not depress K uptake by alfalfa whereas K depressed absorption of Ca regardless of the Ca content in the soil. However, Jones suggested excessive Ca in soils could result in a deficiency of either K or Mg in plants, while high Mg in soils could lead to reduced plant growth due to the imbalance of Ca, K and Mg [16]. It has also been suggested that the uptake of $NH_4^+$ may reduce K uptake by some plants [16]. Therefore, the presence and the concentrations of these competing cations in soil solution can potentially alter the uptake of K by plants from soils.

As sufficient amounts of available K in soil environments are important to satisfy plant growth, soil testing in the presence of other cations is crucial to predict K status in soils before seeding. There are considered to be four defined pools of K in soil, solution K (free $K^+$ in soil solution), exchangeable K ($K^+$ weakly bound by exchange sites), non-exchangeable/slowly exchangeable K (mainly refers to $K^+$ strongly bound by exchange sites or trapped between interlayers of minerals) and mineral K, and these pools are in equilibrium with each other [17,18]. Generally, soil solution K and exchangeable K are considered the most accessible for plant uptake, although it was also found that non-exchangeable K accounted for a large proportion of the total K taken up by plants in a K exhaustion experiment [19]. Wang [20] also reported that mineral K contributed to plant-available K in the presence of root exudates, including oxalic acid, malic acid, tartaric acid or some organic acids, when there was insufficient exchangeable K in soil to satisfy plant demand. Therefore, it is necessary to choose a soil K testing method that measures the appropriate K pool that reflects plant K requirements.

Currently, the most widely used methods for extracting available K from soils are based on the principle of ion exchange, that is, the available K is displaced from soil surfaces using competing cations. The amount of K extracted is dependent on the properties of the ion used to exchange with $K^+$, such as valence, ion size, selectivity, ion concentration, soil to solution ratio, extracting time, temperature, etc., Houba et al. [21] proposed 0.01 M $CaCl_2$ as an extractant for K testing of soils which could be used for practical diagnostic purposes, but acknowledged that this extractant did not remove all exchangeable K from soils, especially clay-rich soils. As an example, Bell et al. [22] reported soil solution K concentration and activity of K in soil solution varied greatly between soil types even when the exchangeable K concentrations (extracted using $NH_4Cl$) were similar. This method using $CaCl_2$ as the extractant was subsequently used by others to predict K status in soils [23–25]. In a glasshouse trial using Guinea grass, Darunsontaya et al. [26] suggested exchangeable K (determined using $NH_4OAc$) was the most suitable method to predict cumulative K uptake by Guinea grass. Wong et al. [27] suggested that the Colwell K method (extracted by $NaHCO_3$) predicted wheat response to K applications on duplex soils moderately well ($R^2 = 0.77$). However, Krishna [14] concluded that predicted response of wheat to K application was soil type and clay content dependent based on exchangeable K values. In addition, Gourley et al. [28] determined critical exchangeable K values to predict pasture response to K fertiliser (at 95% of maximum relative yield) and found the critical values to be soil type dependent. Clearly, traditional methods for measuring available K need to be improved or new methods should be investigated.

The diffusive gradients in thin films (DGT) technique has been successfully used to measure many metal elements in water, sediment and soil [29–31]. Greater accuracy is also found in predicting plant uptake and response to phosphorus (P) fertilisers using the DGT technique compared to traditional extraction methods [32–34], and there is concordance between the pool of P in soils accessed by plants and by the DGT technique [35,36]. Some progress in K measurement using the DGT technique has been achieved. Amberlite IRP-69 was used as the resin gel in the DGT technique to measure K in soils [37], and this resin gel showed a large capacity for K. However, due to the non-evenly distributed Amberlite in the binding gel, some limitations were observed in terms of short deployment time, limited concentration range measurable, and difficulty in applying the resin gel on the DGT device because of the curved shape [37]. Despite these limitations, the authors concluded that the DGT method predicted K uptake of winter barley with similar accuracy to the $NH_4OAc$ K method. The competing effect of Ca on K uptake by the Amberlite gel was also reported to be not significantly influenced at short deployment times (e.g. 2 h) [37]. Zhang et al. [38] optimized the DGT method by using a mixed Amberlite and ferrihydrite (MAF) gel which enabled use of the method for a wider range of conditions in terms of longer deployment time and higher K concentration in solution. However, the effects of the competing cations on K uptake by the MAF gel at longer deployment times are yet to be established. Since the theory of K uptake by the Amberlite contained resin gel is based on ion exchange, the MAF gel has the potential to simultaneously measure Ca and Mg [39]. Measurement of Ca and Mg in fresh water using the DGT has previously been reported [40], but the diffusion coefficients of Ca and Mg through the diffusive gel are not well documented.

This paper investigates the effects of three main cations ($Ca^{2+}$, $Mg^{2+}$ and $NH_4^+$) found in soil solution on K uptake by the MAF gel in the DGT technique in order to provide an accurate analytical tool for measuring Ca, K and Mg simultaneously, with a focus on elution and uptake efficiencies, practical capacity and diffusion coefficients. Furthermore, we aimed to assess the feasibility of using the DGT method for available K measurement in agricultural soils in the presence of varying cation concentrations, and to investigate the performance of the MAF gel for testing Ca, K and Mg simultaneously using the DGT technique.

## 2. Material and methods

### 2.1. Gels and DGT devices preparation

Gel solution contained 0.3% of cross-linker (DGT Research Ltd., UK) and 15% of Acrylamide (Sigma, USA) [30,32]. The diffusive gels (0.6 mm) were prepared according to previously published procedures [30,41]. The mixed Amberlite and ferrihydrite (MAF) gel was prepared according to the procedures described by Zhang et al. [38]. Briefly, 2 g of wet Amberlite (IRP-69 ion-exchange resin, 100–500 wet mesh) and 1 g of ferrihydrite slurry were added to 5 mL gel solution, followed by 30 μL of ammonium persulfate and 12 μL of TEMED (*N*,*N*,*N*′,*N*′-tetramethylethylenediamine). Glass fiber filter papers with a thickness of 0.2 mm (0.45 μm, Toyo Roshi Kaisha, Ltd., Japan) were used on top of the diffusive gel for protection. DGT devices (DGT Research Ltd., Lancaster, UK), with an effective area of 2.54 $cm^2$, were used to load the gel assemblies.

### 2.2. Binding gel blanks and MDL

Five DGT devices containing the MAF gels were used to measure the mass of Ca and Mg on blank gels. The MAF gel was transferred to 1 mL of 1 M HCl for elution. The elution solution was diluted using 9 mL of Milli-Q water before analysis. Concentrations of Ca, K and Mg in the solutions and the eluent were analysed by an inductively coupled plasma-optical emission spectrometer (ICP-OES, PerkinElmer, Optima 7000DV) at λ of 317.933 nm for Ca, 766.490 nm for K and 279.077 nm for Mg. The minimum detection limits (MDL) were calculated according to methods described by Thompson et al. [42], equalling the average of the blank values plus 3 times the standard deviation.

### 2.3. Effects of competing cations on K retention

#### 2.3.1. Effect on elution and uptake efficiencies

Five series of solutions with different concentrations of cations ($K^+$ and competing cations) were used to test the elution and uptake efficiencies. The concentrations and approximate ratios of Ca, K and Mg in the solutions were designed to encompass the ranges found in typical soil solutions [43]:

i. four solutions containing K (as KCl) alone, 5, 10, 20 and 30 mg $L^{-1}$;
ii. four paired solutions containing Ca (as $CaCl_2$) of 5, 10, 15 and 20 mg $L^{-1}$; K of 2.5, 5, 7.5, 10 mg $L^{-1}$;
iii. four paired solutions containing K of 2.5, 5, 7.5, 10 mg $L^{-1}$; Mg (as $MgCl_2$) of 5, 10, 15 and 20 mg $L^{-1}$;
iv. four paired solutions containing K of 2.5, 5, 7.5, 10 mg $L^{-1}$; $NH_4^+$ (as $NH_4Cl$) of 1.25, 2.5, 3.75 and 5 mg $L^{-1}$; and
v. four paired solutions containing Ca of 5, 10, 15 and 20 mg $L^{-1}$, K of 2.5, 5, 7.5, 10 mg $L^{-1}$ and Mg of 1.25, 2.5, 3.75 and 5 mg $L^{-1}$.

Initially 50 mL tubes containing 10 mL of each solution with an MAF gel were placed on an end-over-end shaker for 24 h. The MAF gels were then transferred to 1 mL of 1 M HCl for elution and Ca, K and Mg in the eluent were analysed as outlined above. Since ammonium persulfate was used in the process of making the MAF gel and diffusive gel, $NH_4^+$ was not analysed. Three replicates were used for each treatment for all of the above tests. Elution ($f_e$) and uptake ($f_u$) efficiencies were calculated as described by Zhang et al. [38]:

$$f_e = \frac{c_{Acid} \times 10.265}{M_{Initial} - M_{Final}} \times 100 \quad (1)$$

$$f_u = \frac{M_{Initial} - M_{Final}}{M_{Initial}} \times 100 \quad (2)$$

where $c_{Acid}$ is the measured element concentration in HCl solution after the target element was eluted (mg $L^{-1}$); "10.265" is the dilution factor (mL), calculated as the volume of the MAF gel (0.265 mL) plus 1 mL of HCl and 9 mL of water used for dilution; and $M_{Initial}$ and $M_{Final}$ are the measured amounts of target element in the solution before and after immersion of the MAF gels (μg).

#### 2.3.2. Effects of competing ions on K capacity and diffusion coefficient

Five different solutions (Solutions I–V) containing K and the competing cations were used to test K uptake by the DGT device containing the MAF gel in the presence of competing cations. The concentrations and ratios of Ca, K, Mg and $NH_4^+$ in the solutions were according to the ranges of each element in typical soil solutions [43]:

Solution I: 15 mg $L^{-1}$ K (as KCl);
Solution II: 30 mg $L^{-1}$ Ca (as $CaCl_2$) and 15 mg $L^{-1}$ K;
Solution III: 15 mg $L^{-1}$ K and 30 mg $L^{-1}$ Mg (as $MgCl_2$);
Solution IV: 15 mg $L^{-1}$ K and 5 mg $L^{-1}$ $NH_4^+$ (as $NH_4Cl_2$); and
Solution V: 30 mg $L^{-1}$ Ca, 15 mg $L^{-1}$ K and 5 mg $L^{-1}$ Mg.

The DGT devices containing the MAF gels and diffusive gels were accommodated by plastic holders and they were deployed in a 4 L container filled with one of the above solutions for between 1 and 72 h, with 3 replicates for each deployment period. Solutions were stirred vigorously throughout the experiment and solution temperatures were recorded at regular intervals. Throughout the experiment, 1 mL of solution sample was taken at regular intervals for determination of any element depletion. After deployment, the MAF gels were retrieved and placed in 1 mL of 1 M HCl for elution and diluted with 9 mL of Milli-Q water before analyses (ICP-OES).

#### 2.3.3. Diffusion coefficient calculation

The diffusion coefficient, ($D$, $cm^2\,s^{-1}$), of a given element through the diffusive gel was calculated using Eq. (3) [44]:

$$D = \frac{\text{slope} \times \Delta g}{A \times C_{solution} \times 60} \quad (3)$$

where "slope" is the measured amount of an element on the gel as a function of deployment time (ng $min^{-1}$); $\Delta g$ is the thickness of the diffusive gel (cm); $A$ is the effective sampling area of the DGT device ($cm^2$); $C_{solution}$ is the concentration of the element in solution (ng $cm^{-3}$) and "60" converts the deployment time from minutes into seconds.

The diffusion coefficients at 25 °C through the diffusive gel were converted from the tested value at experimental temperature ($D_t$) according to Eq. (4) [30]:

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

### 2.4. Soil tests

#### 2.4.1. Soil characterisation

Twenty soils representative of broad acre agricultural regions in Australia (Table 1) were dried at 40 °C in an oven to constant weight and sieved to < 2 mm. Soil pH was measured in 0.01 M $CaCl_2$ solution in a soil to solution ratio of 1:5 [45]. Total organic carbon was measured according to the method provided by Rayment and Higginson [45]. Exchangeable Ca, Mg and cation exchange capacity (CEC) were extracted using 1 M $NH_4Cl$ [45]. Particle size was determined using the method described by Boman and Hutka [46].

**Table 1**
Physical and chemical properties of the Australian agricultural soils used in this study.

| Site | Abbreviation | State | pH | TOC (%) | Exchangeable Ca (mg kg$^{-1}$) | Exchangeable Mg (mg kg$^{-1}$) | Exchangeable K (mg kg$^{-1}$) | Exchangeable Ca:Mg:K | Solution Ca:Mg:K | CEC (cmol (+) kg$^{-1}$) | Clay (%) | Silt (%) | Sand (%) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Boyup Brook | BB | WA | 5.8 | 3.0 | 1818 | 54 | 57 | 32:1:1 | 23:2:1 | 10.1 | 3.8 | 2.5 | 87 |
| Birchip | BC | VIC | 7.1 | 0.7 | 8584 | 1052 | 603 | 14:2:1 | 15:2:1 | 30.5 | 43.0 | 8.5 | 43 |
| Black Point | BP | SA | 7.3 | 1.6 | 4505 | 487 | 388 | 12:1:1 | 6:1:1 | 18.0 | 16.9 | 12.6 | 67 |
| Boathaugh | BT | WA | 6.0 | 1.7 | 736 | 463 | 159 | 5:3:1 | 0.4:0.5:1 | 8.9 | 20.6 | 8.8 | 64 |
| Condobolin | CN | NSW | 5.7 | 1.2 | 1794 | 510 | 729 | 2:1:1 | 0.3:0.2:1 | 14.7 | 27.6 | 12.1 | 57 |
| Ilanson | IN | SA | 6.3 | 1.5 | 2286 | 177 | 261 | 9:1:1 | 8:1:1 | 8.2 | 13.1 | 24.1 | 59 |
| Karoonda | KD | SA | 6.4 | 0.4 | 728 | 87 | 71 | 10:1:1 | 4:1:1 | 4.5 | 2.4 | 0.4 | 96 |
| Karri Loam | KL | WA | 6.1 | 4.1 | 1811 | 443 | 209 | 9:2:1 | 1:0.4:1 | 11.2 | 7.2 | 8.9 | 73 |
| Koppio | KP | SA | 6.8 | 3.9 | 1954 | 496 | 312 | 6:2:1 | 1:0.2:1 | 12.2 | 14.7 | 10.7 | 67 |
| Kelly | KY | NSW | 7.3 | 1.1 | 15379 | 4697 | 746 | 21:6:1 | 7:3:1 | 67.0 | 52.3 | 23.5 | 17 |
| Langhorne Creek | LC | SA | 6.7 | 0.8 | 1653 | 144 | 189 | 9:1:1 | 2:0.3:1 | 7.1 | 4.1 | 1.4 | 92 |
| Lochearn | LN | NSW | 7.0 | 0.7 | 8639 | 1490 | 732 | 12:2:1 | 4:0.9:1 | 32.1 | 35.4 | 25.6 | 35 |
| Mount Damper | MD | SA | 6.6 | 0.5 | 1276 | 112 | 87 | 15:1:1 | 5:0.8:1 | 6.2 | 3.5 | 0.7 | 94 |
| Mudamuckla | MK | SA | 7.6 | 0.7 | 2741 | 174 | 422 | 6:0.4:1 | 4:0.4:1 | 8.1 | 5.9 | <0.1 | 94 |
| Ngarkat | NK | SA | 6.6 | 0.7 | 976 | 69 | 37 | 26:2:1 | 2:0.4:1 | 4.6 | 2.1 | 1.1 | 95 |
| Northam | NM | WA | 5.2 | 1.4 | 348 | 63 | 89 | 4:1:1 | 1:0.2:1 | 6.0 | 8.2 | 3.5 | 86 |
| Pt. Kenny | PK | SA | 7.5 | 2.9 | 4716 | 409 | 486 | 10:1:1 | 3:0.4:1 | 13.1 | 9.9 | 3.7 | 24 |
| Stansbury | SB | SA | 5.7 | 1.1 | 847 | 88 | 20 | 43:4:1 | 1:0.3:1 | 5.2 | 1.7 | 0.8 | 95 |
| Wharminda | WD | SA | 6.4 | 0.9 | 766 | 208 | 184 | 4:1:1 | 0.4:0.2:1 | 4.4 | 2.9 | 0.5 | 95 |
| Walpeup LTP | WL | VIC | 6.8 | 0.5 | 1920 | 394 | 408 | 5:1:1 | 1:0.3:1 | 10.0 | 8.7 | 3.2 | 86 |

*2.4.2. Soil K measurements using different methods and effects of competing cations on DGT K uptake in soils*

Soils (approximately 50 g) were gradually wetted to saturation point (assessed visually) and left overnight to equilibrate elements in soil solution and soil solid phase before deploying the DGT devices that had been prepared as described above. After 24 h deployment, the devices were dismantled and the MAF gels were placed into 1 mL 1 M HCl for elution. Three replicates were used for each soil. Concentrations of Ca, K and Mg in the eluent were measured after dilution using Milli-Q water by an ICP-OES as outlined above. Concentrations of Ca, K and Mg determined using DGT ($C_{DGT}$) were calculated by Eq. (5):

$$C_{DGT} = \frac{M\Delta g}{DAt} \quad (5)$$

where $C_{DGT}$ is the concentration of element measured by DGT; $M$ is measured amount of element on gel; and $t$ is the deployment time ($s$).

Solution K was extracted by Rhizon™ samplers [47,48]. Colwell K was extracted by 0.5 M $NaHCO_3$ [45] and exchangeable K was extracted by 1 M $NH_4OAc$ [45]. All methods were carried out in triplicate for each soil. Potassium extracted by $NaHCO_3$ was determined by flame photometry (Sherwood Model 420, UK) due to high $NaHCO_3$ amounts interfering with the plasma generation of the ICP-OES; Concentrations of other elements in the extractants were determined using ICP-OES as outlined before.

*2.5. Statistical analysis*

Analysis of variance (ANOVA) was performed using GENSTAT 14th edition to assess whether the K elution and uptake efficiencies were significantly different from each other between treatments.

## 3. Results and discussion

*3.1. Binding gel blanks and MDL*

The measured blank mass of K on the MAF gel was previously reported to be 7.9 ± 0.03 μg device$^{-1}$, and the minimum detection limit (MDL) was 8.2 μg device$^{-1}$ using an ICP-OES [38]. The MDLs of the MAF gel for Ca and Mg were 4.16 and 3.16 μg device$^{-1}$, respectively.

*3.2. Effects of competing cations on K retention*

*3.2.1. Effects on elution and uptake efficiencies*

Potassium elution efficiencies measured were stable in solutions with or without the competing cations, with no significant difference at $P \leq 0.05$ between treatments (Table 2), indicating no effect of competing cations on elution efficiency of the MAF gel for K. In order to accurately measure K retained by the DGT device using the MAF gel and HCl as the elution agent, an average of 85% is recommended for K testing in soils using the DGT technique. The uptake efficiencies of the MAF gel for K decreased from 99% in Solution iv ($NH_4^+$) to 86% in Solution iii (Mg). However, the decrease in uptake efficiency was due to the decreased values

**Table 2**
Elution efficiencies ($f_e$) and uptake efficiencies ($f_u$) of the MAF gel for cations in different solutions (i, solutions containing $K^+$ alone; ii, solutions containing $Ca^{2+}$ and $K^+$; iii, solutions containing $K^+$ and $Mg^{2+}$; iv, solutions containing $K^+$ and $NH_4^+$; and v, solutions containing $Ca^{2+}$, $K^+$ and $Mg^{2+}$, refer to Section 2.3.1). Mean values in a column with same letters are not significantly different ($P \leq 0.05$, $n = 3$). SD means standard deviation.

| Solution | $f_e$ | | $f_u$ | |
|---|---|---|---|---|
| | Mean (%) | SD | Mean (%) | SD |
| K | | | | |
| i | 84a | 1.8 | 96a | 2.5 |
| ii | 85a | 1.9 | 93ab | 4.5 |
| iii | 85a | 3.0 | 86b | 8.9 |
| iv | 84a | 2.7 | 99a | 2.2 |
| v | 85a | 2.0 | 91ab | 5.4 |
| Average | 85 | 2.3 | 93 | 4.7 |
| Ca | | | | |
| ii | 47a | 3.7 | 100a | 0.1 |
| v | 47a | 2.3 | 100a | 0.1 |
| Average | 47 | 3.0 | 100 | 0.1 |
| Mg | | | | |
| iii | 63a | 6.2 | 100a | 0.2 |
| v | 61a | 2.1 | 100a | 0.8 |
| Average | 62 | 4.1 | 100 | 0.5 |

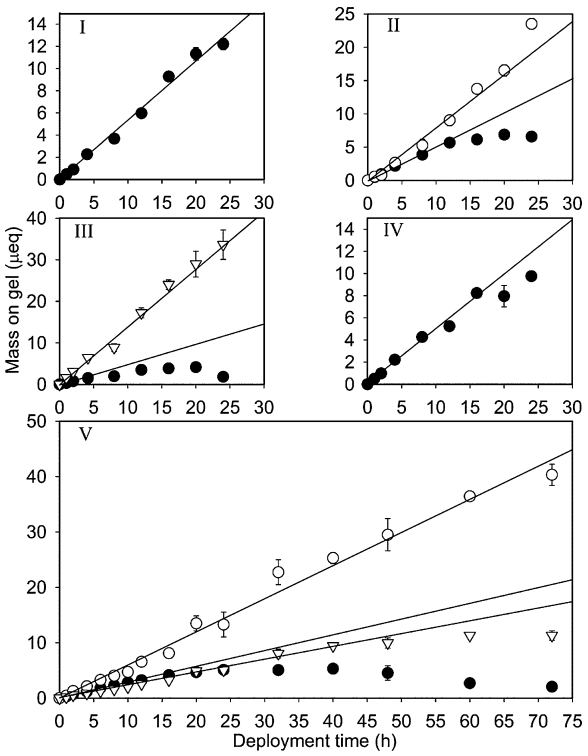


**Fig. 1.** Measured mass of cations on the MAF gel in different solutions: I, 15 mg $L^{-1}$ K; II, 30 mg $L^{-1}$ Ca and 15 mg $L^{-1}$ K; III, 15 mg $L^{-1}$ K and 30 mg $L^{-1}$ Mg; IV, 15 mg $L^{-1}$ K and 5 mg $L^{-1}$ $NH_4^+$; and V, 30 mg $L^{-1}$ Ca, 15 mg $L^{-1}$ K and 5 mg $L^{-1}$ Mg (● represents the mass of K on the MAF gel, ○ represents the mass of Ca on the MAF gel and ▽ represents the mass of Mg on the MAF gel). Error bars represent the standard errors of three replicates.

obtained for the two highest concentrations of Solution iii (Mg) and the highest concentration of Solution v (Ca + Mg), where the mass of cations on the MAF gel suggested restriction of K uptake occurred compared to the mass limit established in cation competition experiments in solution (Fig. 1, Table 4). The uptake ability of the MAF gel for K is impaired when the MAF gel absorbs sufficient amounts of $Ca^{2+}$ and/or $Mg^{2+}$, even though the practical capacity of the MAF gel for K (450 μg as reported by Zhang et al. [38]) has not been reached. The theory of the DGT technique holds when the uptake efficiency equals 100% and infinite sink conditions are present in order to maintain a concentration gradient through the diffusive gel. In a soil deployment using the MAF gel, the uptake of K and cations are controlled by the thickness of diffusive gel and deployment time. Therefore, all the cations in soil solution are not necessarily taken up by the MAF gel during a soil deployment. Consequently, the effects of Ca and Mg on K uptake efficiency may occur only in soils with extremely high soluble Ca and Mg content and/or a long deployment time.

The elution efficiencies of the MAF gel for Ca and Mg averaged 47% and 62%; the uptake efficiencies averaged 100% (Table 2). Compared to the elution and uptake efficiencies of the MAF gel for K, the lower efficiencies and higher uptake efficiencies for Ca and Mg suggest the MAF gel has greater selectivity for binding $Ca^{2+}$ and $Mg^{2+}$ compared to $K^+$.

### 3.2.2. Uptake of cations by the MAF gel

The mass of K accumulated by the MAF gels increased with deployment time linearly up to 24 h in 15 mg $L^{-1}$ K solution ($R^2$ = 0.99, Fig. 1I), with a maximum of 12.2 μeq of K accumulated on the MAF gel, which was in good agreement with the previous defined practical capacity of the MAF gel for K (11.5 μeq) reported by Zhang et al. [38]. However, the linear accumulation of K by the MAF gel over time was affected by solutions containing competing cations (Solution II–V, Fig. 1II–V). The upper limit for concentrations of K on the gel where linear accumulation occurred were 5.7 μeq at 12 h, 1.5 μeq at 4 h, 8.2 μeq at 16 h and 4.2 μeq at 16 h in Solutions II–V, respectively (Fig. 1II–V). In the presence of a higher concentration of Ca in solution compared to K and Mg, the amount of K and Mg on the binding gel reached 4.2 μeq and 9.4 μeq respectively, before the linear uptake rate was compromised. It can be concluded that the maximum mass of K accumulated on the MAF gel that is linear with deployment time is dependent on the concentration of Ca and Mg in the solution. However, the uptake of K remains linear over short deployment periods as long as the mass of K does not reach the practical capacity and the mass of the competing cations do not reach a certain level on the MAF gel simultaneously. In presence of Ca in the solution alone, a combined mass of 14.7 μeq of Ca and K on the MAF gel resulted in insufficient binding sites on the Amberlite for K (Fig. 1II); in the presence of Mg in the solution, a combined mass of 7.9 μeq of K and Mg resulted in insufficient binding sites on the Amberlite for K (Fig. 1III); alternatively, a total mass of 15.5 μeq of Ca, K and Mg together indicates insufficient binding sites on the Amberlite for K (Fig. 1V).

Comparing the effects of Ca and Mg on K uptake by the MAF gel, it appears that K was displaced from the MAF gel and diffused

**Table 3**
Diffusion coefficients (D) of Ca, K and Mg in different solutions at 25 °C (I, 15 mg $L^{-1}$ K; II, 30 mg $L^{-1}$ Ca and 15 mg $L^{-1}$ K; III, 15 mg $L^{-1}$ K and 30 mg $L^{-1}$ Mg; IV, 15 mg $L^{-1}$ K and 5 mg $L^{-1}$ $NH_4^+$; and V, 30 mg $L^{-1}$ Ca, 15 mg $L^{-1}$ K and 5 mg $L^{-1}$ Mg). *N* represents the number of effective deployment times.

| Element | Solution | Competing ion | $R^2$ | $D_{25}$ ($cm^2 s^{-1}$) | *N* |
|---|---|---|---|---|---|
| K | I | None | 0.987 | $1.31 \times 10^{-5}$ | 9 |
| K | II | $Ca^{2+}$ | 0.995 | $1.15 \times 10^{-5}$ | 6 |
| K | III | $Mg^{2+}$ | 0.997 | $0.98 \times 10^{-5}$ | 4 |
| K | IV | $NH_4^+$ | 0.983 | $1.17 \times 10^{-5}$ | 7 |
| K | V | $Ca^{2+}$, $Mg^{2+}$ | 0.977 | $1.12 \times 10^{-5}$ | 9 |
| Ca | II | $K^+$ | 0.971 | $0.54 \times 10^{-5}$ | 9 |
| Ca | V | $K^+$, $Mg^{2+}$ | 0.988 | $0.56 \times 10^{-5}$ | 16 |
| Mg | III | $K^+$ | 0.993 | $0.55 \times 10^{-5}$ | 9 |
| Mg | V | $Ca^{2+}$, $K^+$ | 0.989 | $0.53 \times 10^{-5}$ | 13 |

**Table 4**
Assessment of the binding limit of the MAF gel for K in the presence of other cations in 20 agricultural soils in Australia after 24 h deployment according to: (1) mass K; (2) mass Ca; (3) mass Mg; and (4) mass total (Ca + K + Mg). "×" indicates where K uptake by the MAF gel was affected by excessive accumulation of cations when the mass/combined mass exceeded the theoretical limit (according to Fig. 1I–III and V).

| Soil abbreviation | Mass K (μeq) | Mass Ca (μeq) | Mass Mg (μeq) | Mass total (μeq) |
|---|---|---|---|---|
| BB | 0.2 | 4.5 | 0.5 | 5.2 |
| BC | 0.5 | 23.9× | 5.2 | 29.7× |
| BP | 1.0 | 7.1 | 1.8 | 9.9 |
| BT | 2.0 | 0.7 | 1.6 | 4.3 |
| CN | 5.7 | 2.0 | 1.5 | 9.2 |
| IN | 1.7 | 36.0× | 5.2 | 43.0× |
| KD | 1.4 | 4.5 | 2.0 | 7.8 |
| KL | 1.7 | 1.5 | 1.5 | 4.8 |
| KP | 3.5 | 2.6 | 1.1 | 7.2 |
| KY | 0.6 | 12.8× | 7.8× | 21.2× |
| LC | 3.1 | 6.5 | 1.6 | 11.2 |
| LN | 1.2 | 13.7× | 4.6 | 19.5× |
| MD | 0.7 | 4.7 | 0.9 | 5.9 |
| MK | 3.1 | 18.2× | 2.6 | 23.9× |
| NK | 0.4 | 1.0 | 0.3 | 1.6 |
| NM | 1.3 | 0.7 | 0.3 | 2.2 |
| PK | 2.1 | 12.9× | 2.7 | 17.6× |
| SB | 1.2 | 1.0 | 0.3 | 2.6 |
| WD | 3.3 | 2.1 | 1.7 | 7.1 |
| WL | 3.8 | 6.6 | 2.5 | 12.9 |
| Theoretical limit | 11.5 | 10.5 | 5.7 | 15.5 |

back into the solution after 20 h deployment in the solution containing 30 mg $L^{-1}$ Mg (Fig. 1III), while the phenomenon of K displacement was minimal in the solution containing the same concentration of Ca (Fig. 1II). When Ca and Mg are present with the same concentration in milligrams per litre in solution, the concentration of Mg in equivalent per litre is 1.7 times that of Ca in solution. This explains why K uptake by the MAF gel was restricted more in the solution containing Mg than that containing Ca in the same concentrations in milligrams per litre (Fig. 1II and III). Preferential absorption of $Ca^{2+}$ and $Mg^{2+}$ over $K^{+}$ by the MAF gel is in agreement with the general rules of cation selectivity associated with valence and hydrated size [49,50]. Tandy et al. [37] deployed the DGT device containing Amberlite gel in solutions containing both Ca and K and concluded that K uptake by the Amberlite gel was not significantly affected by concentrations of Ca usually found in fertile soils at 2 h deployment. However, the effect of Ca on K uptake longer than 2 h still needs to be investigated. It appears the effect of $NH_4^+$ on K uptake in a DGT soil test is negligible, and since $NH_4^+$ is not a major cation in soils [12] it is not discussed further.

On the contrary, the presence of K in solution had no effect on the uptake of Ca and Mg by the MAF gel. The mass of Ca and Mg accumulated by the MAF gel increased linearly with deployment time (Fig. 1II, III and V), except for Mg uptake after 40 h deployment in Solution V. The practical capacity of the MAF gel for Ca and Mg were at least 40.3 μeq and 33.6 μeq, respectively (Fig. 1V and III), which is much higher than the practical capacity of the MAF gel for K alone. Therefore, the effect of K on uptake of Ca and Mg by the

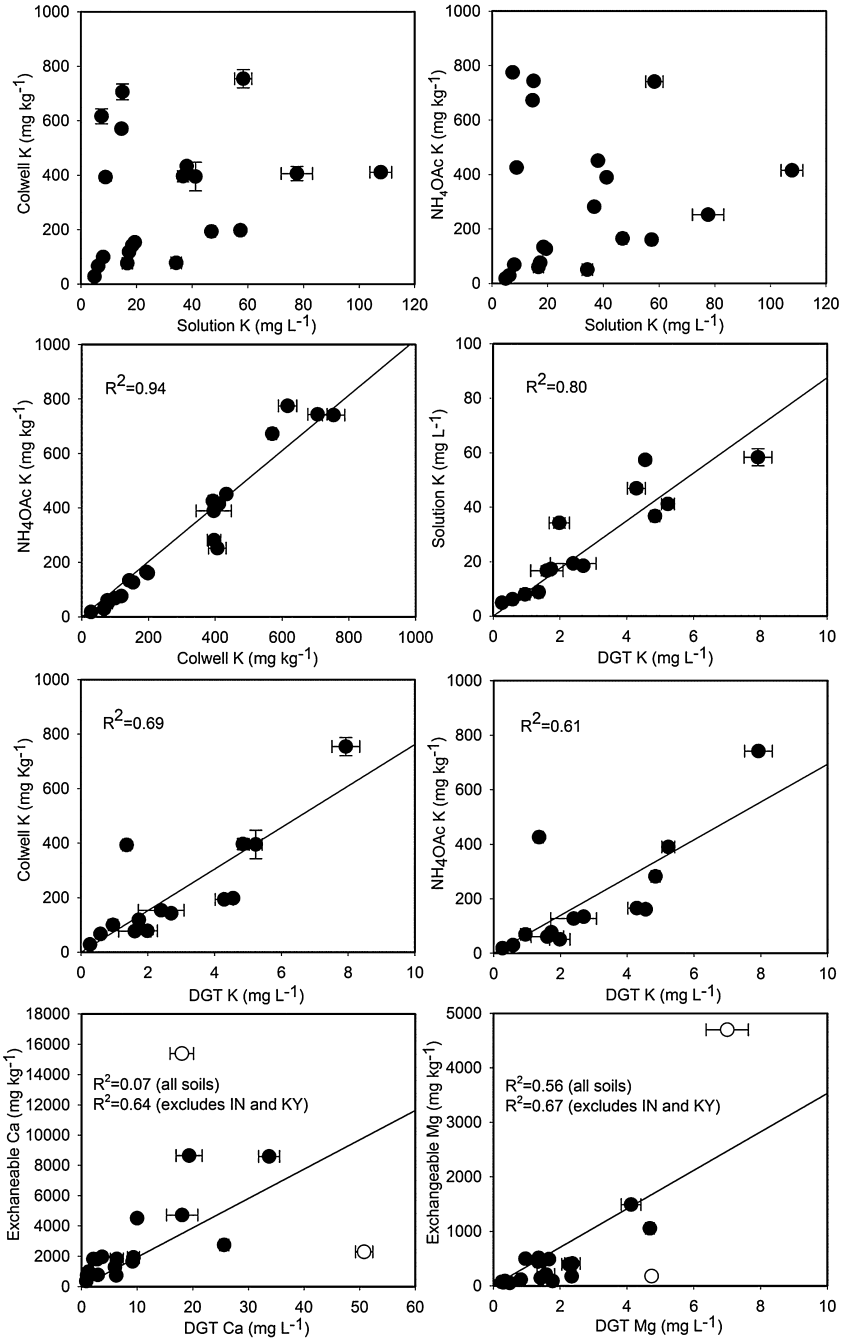


**Fig. 2.** Correlation between concentrations of K extracted using different methods (the values excludes the ones having excessive mass of cations on the MAF gel in a DGT test indicated by theoretical limits in Table 4; values of exchangeable Ca and Mg in open circle are from soils IN and KY). Error bars represent the standard errors of three replicates.

MAF gel is negligible due to the comparatively weak binding ability of K to the Amberlite.

*3.2.3. Recommended diffusion coefficients for Ca, K and Mg testing in soils*

Based only on the linear uptake of K with deployment time in solution, the K diffusion coefficient in Solution I was $1.31 \times 10^{-5}$ $cm^2\,s^{-1}$ at 25 °C (Table 3), which was similar to that found previously [38]. Calculated K diffusion coefficients in solutions with competing cations were lower than the diffusion coefficient in K solution alone but were similar across the competing cations (Table 3). To accurately measure available K in soils using the DGT method, an effective diffusion coefficient of $1.12 \times 10^{-5}$ $cm^2\,s^{-1}$ at 25 °C (Solution V) is recommended as Ca and Mg are the major competing cations present in agricultural soils.

Due to a higher affinity of Ca and Mg for the Amberlite in the MAF gel compared to K, the effect of K on diffusion coefficients of Ca and Mg is presumed to be negligible. Therefore, the diffusion coefficients of Ca and Mg through the diffusive gel were $0.56 \times 10^{-5}$ and $0.53 \times 10^{-5}$ $cm^2\,s^{-1}$ at 25 °C (Table 3), 71% and 75% of the diffusion coefficient values obtained in water for Ca and Mg reported by Li and Sandra [51], respectively. The decreased coefficients of Ca and Mg in the diffusive gel are presumably due to a restriction from the diffusive gel.

*3.3. Soil tests*

*3.3.1. Uptake of K by DGT from soils*

Based on a 24 h deployment time using a 0.6 mm diffusive gel (excluding the thickness of filter paper), the accumulated K on the MAF gel varied from 0.2 to 5.7 μeq in a wide range of Australia broad acre agricultural soils (Table 4). The maximum amount of K accumulated by the MAF gel was far lower than the practical capacity of the MAF gel for K alone which is 11.5 μeq as reported by Zhang et al. [38]. However, the measured mass of Ca on the MAF gel would have been sufficient to generate non-linear uptake of K by the DGT devices deployed for less than 24 h in some soils. Compared to the mass of Ca on the MAF gel in Fig. 1II, K uptake by the MAF gel was affected by excessive Ca in 30% of the agricultural soils sampled. The presence of $Ca^{2+}$ in soils could therefore pose a significant problem of non-linear uptake of K by the DGT using a traditional 24 h deployment, potentially causing underestimation of the amount of K which could be accumulated by the DGT device (in the absence of ion competition). Potential effects of cations on K binding ability of the MAF gel assessed by the mass of Ca was the same to the combined mass of Ca, K and Mg (Table 4). In contrast, only soil KY (5%) was found to have a mass Mg of 7.8 μeq on the MAF gel which was larger than the theoretical mass limit of Mg. The problem of non-linear uptake of K caused by the presence of cations therefore appears mainly driven by high concentrations of Ca in soil solutions. However, the DGT method (a traditional 24 h deployment) can still be used to measure K in agricultural soils when the concentrations of Ca and Mg are not exceptionally high, but using shorter deployment times could possibly alleviate the competing effects on K based on the theory of element uptake by a DGT binding gel. To avoid the potential influence of $NH_4^+$ on K uptake by the MAF gel, it is suggested that soil samples should not be taken shortly after application of ammonium fertilizer.

*3.3.2. Comparison of soil K extracted by DGT and traditional methods*

In theory, the DGT method can measure both solution K and part of the K resupplied from the soil solid phase. Lack of any significant relationship between soil solution K with either Colwell K or $NH_4OAc$ K suggested the soil available K pools measured by these methods are quite different (Fig. 2). A strong linear relationship between Colwell K and $NH_4OAc$ K ($y = 1$, $R^2 = 0.94$, $P < 0.001$) indicates that the Colwell method is effectively extracting the exchangeable K pool in these soils. The correlation between DGT K and solution K was significant ($R^2 = 0.80$, $P < 0.001$), and the correlation was moderate with the other two methods ($R^2 = 0.69$, $P < 0.001$ – Colwell K and $R^2 = 0.61$, $P < 0.001$ – $NH_4OAc$ K, Fig. 2). Values where K uptake by the MAF gel was affected by excessive amounts of competing cations were not presented. The good correlation with solution K and moderate correlation with exchangeable K methods suggest that in some circumstances DGT measures a different K pool compared to Colwell K and $NH_4OAc$ K methods, and is most closely associated with the soil solution K measurement. Poor correlation was found between DGT Ca and exchangeable Ca ($R^2 = 0.07$, $P = 0.053$), but moderate correlation was found between DGT Mg and exchangeable Mg ($R^2 = 0.56$, $P < 0.001$). The correlation between DGT Ca and exchangeable Ca was improved ($R^2 = 0.64$, $P < 0.001$) when soils IN and KY were excluded. However, the mechanism of causing the improved correlation is not clear. The moderate correlation between DGT Ca and exchangeable Ca, DGT Mg and exchangeable Mg suggests DGT also measures different proportions of the exchangeable pools of Ca and Mg in soils.

## 4. Conclusions

The effects of the major competing cations ($Ca^{2+}$, $Mg^{2+}$ and $NH_4^+$) on K uptake by the mixed Amberlite and ferrihydrite (MAF) gel were investigated in order to ensure accurate K measurements using the DGT technique. There was no difference ($P \leq 0.05$) between the elution and uptake efficiencies of the MAF gel for K in the presence of these competing cations when the amount of these cations did not exceed the mass limit established for K. Lower diffusion coefficients for K in the presence of competing cations were observed compared to the coefficients in K solution alone, but the coefficients measured in solutions with different competing cations were in good agreement with each other. To accurately measure soil K using the DGT technique, the recommended diffusion coefficient of K through the diffusive gel for soil K testing was $1.12 \times 10^{-5}$ $cm^2\,s^{-1}$ at 25 °C. Using 20 typical Australian agricultural soils and a DGT deployment time of 24 h, $Ca^{2+}$ in soil solutions was found to interfere with K uptake by the MAF gel in 30% of the soils. However, this problem could potentially be avoided by using a shorter deployment time. It is also recommended that in all cases Ca and Mg accumulated by DGT are measured to ensure an infinite sink condition is present for K. The DGT method provides a measure more closely related to soil solution K rather than exchangeable K. Further work is required to assess whether the DGT method for K correlates with the plant available K pool in various soil types. As the elution efficiencies and diffusion coefficients of Ca and Mg were clearly defined in this work, the MAF gel has the potential to measure Ca and Mg simultaneously.

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# CHAPTER 4

## Diffusional supply of elements from the soil solid phase to the DGT surface: effects of deployment time and thickness of the diffusive gel on calcium, potassium, magnesium and phosphorus uptake by the DGT

This chapter will be submitted to Plant and Soil.

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| Signature | | Date | |

**Abstract**

*Background and aims* The diffusive gradients in thin films (DGT) has been developed to allow simultaneous measurement of calcium (Ca), potassium (K), magnesium (Mg) and phosphorus (P) in agricultural soils using a mixed Amberlite and ferrihydrite (MAF) gel. However, the effects of deployment time and thickness of the diffusive gel on measured $C_{DGT}$ for these elements are not clear. This study investigated the effects of deployment time and thickness of the diffusive gels on measured $C_{DGT}$ for Ca, K, Mg and P in agricultural soils.

*Methods* DGT devices containing the MAF gels and diffusive gels (0.6 mm or 1.2 mm) were deployed on 5 soils for different deployment periods.

*Results* Measured $C_{DGT}$ changed with deployment time in the order of K>Ca=Mg>P, while $C_{DGT}$ of P might be relatively stable with deployment time. The changing of $C_{DGT}$ for K in different soils with deployment times indicated K resupply ability of those soils to soil solutions. The effects of applied thickness of the diffusive gel on $C_{DGT}$ varied across soils. To some extent, thicker diffusive gels can alleviate the competing effects on K uptake by the MAF gel due to lowered K flux through the diffusive gel.

*Conclusions* In the aspect of DGT, the deployment time and applied diffusive gels had greater effect on $C_{DGT}$ of K compared to other elements tested. Deployment time and thickness of diffusive gel should be modified while correlating $C_{DGT}$ of K to plant K uptake from soils.

**Keywords** Deployment time, DGT, Diffusion, Potassium, Soil testing, Thickness

## Introduction

In the previous chapters (Chapters 2 and 3), the resin gel for potassium (K) testing using the DGT method was optimized, and the effects of competing cations on K uptake by the DGT was initially investigated. Calcium (Ca) present in some Australian agricultural soils was reported to be the main competing cation of the mixed Amberlite and ferrihydrite (MAF) gel for K uptake in the DGT technique using a 24 h deployment time. However, the competition effects could potentially be alleviated by using shorter deployment times. To investigate the MAF gel to measure Ca, K, magnesium (Mg) and phosphorus (P) simultaneously with respect to plant availability, it is imperative to understand the relationship between measured $C_{DGT}$ values of these elements with deployment time and thickness of the diffusive gel.

Before measuring the available fraction of an element in soils using the DGT method, soils are always saturated with water and the element is allowed to equilibrate between soil solution and the soil solid phase. The target element in soil solution diffuses towards the sink through the diffusive gel and then is accumulated on the resin gel within a certain deployment time. The time averaged $C_{DGT}$ reflects both element concentration in soil solution and that resupplied from the soil solid phase. Therefore, the resupply of an element is dependent on both the amount absorbed on the soil solid phase and the desorption rate of the element from the soil solid phase to replenish the soil solution, due to a lowered concentration induced on the DGT surface (Ernstberger et al. 2002; Harper et al. 1998). The factors affecting $C_{DGT}$ can be categorized into two groups: 1) diffusional resupply of the element from the soil solid phase to soil solution, controlled by specific element behavior and soil properties; and 2) changes in element resupply induced by DGT parameters. To further investigate how the measured $C_{DGT}$ is affected by element and soil properties when DGT is deployed on the soil surface, distribution coefficients ($K_D$) and response times ($T_C$) were

defined to describe the interaction of DGT with soils (Ernstberger et al. 2002; Ernstberger et al. 2005; Harper et al. 1998; Lehto et al. 2008), where $K_D$ reflects the distribution of element between the solid phase and solution; $T_C$ is the time needed for element equilibration between the soil solid phase and solution. Providing the characteristics of the diffusive gel remains the same when a standard DGT device is used, $K_D$ and $T_C$ are then dependent on element and soil properties.

The deployment time and thickness of the diffusive gel are two factors that can affect the element dynamics in a soil system that is induced by DGT, assuming the diffusive gels are made of the same material. The measured $C_{DGT}$ can be dependent on the deployment time in a soil test if resupply is low and unable to sustain solution concentrations. The ratio (R) of $C_{DGT}$ to the initial concentration in soil solution is used to interpret the depletion of an element by the DGT from soil solution (Harper et al. 1998). The measured R values for $C_{DGT}$ of cadmium (Cd), nickel (Ni) and zinc (Zn) have been shown to rapidly increase and then decrease with increasing deployment time on soil samples (Ernstberger et al. 2005). The initial increase of R with deployment time reflects the establishment of the diffusive gradient process in the diffusive gel, and then the decreasing trend reflects a quicker uptake rate of element from the DGT device than can be supplied from adjacent soil solid phases, indicating a poor resupply ability of the element from soil solid phase to soil solution. The changes of measured element concentration ($C_{DGT}$) using the DGT with deployment time are similar to the changes of the ratio R with deployment time, as the initial soil concentration is the same for each soil, but the concentration measured by DGT varies with time.

The concentration of an element measured by DGT may differ with the thickness of diffusive gels due to changed flux through the diffusive gel. Previous work assessing the relationship of the DGT-induced flux with thickness of the diffusive gel has been extensively discussed

(Gaabass et al. 2009; Scally et al. 2003; Zhang and Davison 1995; Zhang et al. 1998b). There was an inverse proportion relationship of the mass of Cd and manganese (Mn) with the thickness of the diffusive gel measured in sediment as described in previous research (Zhang and Davison 1995). Increased fluxes of Cd, copper (Cu), Ni and Zn with reciprocal values of the diffusive gel thickness were also found in DGT soil deployment experiments (Zhang et al. 1998b). Increased values of $C_{DGT}$ of labile Cd, Cu and lead (Pb) were observed with increased thickness of diffusive gels in solution deployment, as increased thickness of the diffusive gel allowed more time for available metal complexes to dissociate, resulting in increased labile concentrations of these metals (Gaabass et al. 2009). When the measured labile metal is kinetically limited, the DGT measured concentration increases with the increase of the thickness of diffusive gels (Scally et al. 2003).

The kinetics of metals measured by DGT in soils has been extensively studied, but the resupply of Ca, K, Mg and P from soil solid phase to the DGT is not well documented. The investigation of the relationship of measured $C_{DGT}$ with deployment time and thickness of the diffusive gel will help understand the relationship between $C_{DGT}$ and factors affecting concentrations of elements accumulated by DGT, thereby optimizing deployment conditions of the DGT technique for precisely predicting plant requirement of these nutrients in soils. The aim of this research was initially to investigate the effects of deployment time and thickness of the diffusive gel on the measured values of $C_{DGT}$ for Ca, K, Mg and P in selected Australian agricultural soils.

## Material and methods

### Preparation of gels and DGT devices

Gel solution was prepared with 0.3% of cross-linker (DGT Research Ltd., UK) and 15% Acrylamide (Sigma, USA). Diffusive gels of 0.6 mm thickness were made according to

previously described procedures (Mason et al. 2005; Zhang and Davison 1995). Diffusive gels of 1.2 mm thickness were prepared using similar procedures to those for making the 0.6 mm gels, by simply using two spacers when the gel solution was cast. The preparation of the mixed Amberlite and ferrihydrite (MAF) gel was performed as described elsewhere (Zhang et al. 2013), briefly it contained 2 g of wet Amberlite (IRP-69 ion-exchange resin, 100-500 wet mesh) and 1 g of ferrihydrite slurry in 5 mL gel solution, plus 30 μL of ammonium persulfate and 12 μL of TEMED (*N,N,N',N'*-Tetramethylethylenediamine). Glass fiber filter papers with a thickness of 0.2 mm (0.45 μm, Toyo Roshi Kaisha, Ltd., Japan) were used throughout the experiment. Plastic DGT devices (DGT Research Ltd, Lancaster, UK) were used to load the gel assemblies.

Soil characterization

Five soils from agricultural regions in Australia (Table 1) were dried at 40 $^{o}$C to constant weight and sieved to < 2 mm. Soil pH was measured in 0.01 *M* $CaCl_2$ solution in a soil to solution ratio of 1:5 (Rayment and Higginson 1992). Total organic carbon was measured according to Rayment and Higginson (1992). Exchangeable Ca, K, Mg and cation exchange capacity (CEC) were determined using 1 *M* $NH_4OAc$ (Rayment and Higginson 1992). Phosphorus buffering index (PBI) was measured using the method described by Moody (2007). When 1000 mg $kg^{-1}$ P was added to soils as ($KH_2PO_4$) to measure PBI, 1280 mg $kg^{-1}$ K was added to the soils at the same time. Potassium buffering ability (KBA) was derived from the PBI test, expressed as mg K absorbed per kilogram soil from the solution. Potassium in the solution was analysed by an inductively coupled plasma-optical emission spectrometer (ICP-OES, PerkinElmer, Optima 7000DV) at λ of 766.490 nm. The amounts of K adsorbed were assumed mostly correlating to the ability of soils for binding K, therefore reflecting K buffering ability of soils. Particle size was determined using the method described by Bowman and Hutka (2002).

**Table 1** Basic properties of the Australian agricultural soils used.

| Site | Abbreviation | State | pH | TOC (%) | Exchangeable Ca (mg $kg^{-1}$) | Exchangeable K (mg $kg^{-1}$) | Exchangeable Mg (mg $kg^{-1}$) | CEC (cmol $kg^{-1}$) | KBA (mg $kg^{-1}$) | PBI[a] | Clay (%) | Silt (%) | Sand (%) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Condobolin | CN | NSW | 5.7 | 1.2 | 1794 | 729 | 510 | 15 | 25 | 85 | 28 | 12 | 57 |
| Ilanson | IN | SA | 6.3 | 1.5 | 2286 | 261 | 177 | 8 | 103 | 56 | 13 | 24 | 59 |
| Gindie | GA | QLD | 6.5 | 0.6 | 3673 | 51 | 1724 | 17 | 745 | 115 | 66 | 14 | 21 |
| Kelly | KY | NSW | 7.3 | 1.1 | 15379 | 746 | 4697 | 67 | 820 | 175 | 52 | 24 | 17 |
| Ngarkat | NK | SA | 6.6 | 0.7 | 976 | 37 | 69 | 5 | 31 | 25 | 2 | 1 | 96 |

[a] PBI was calculated as (Ps+initial Colwell P)/$c^{0.41}$, where c is the final P concentration in solution in mg $L^{-1}$.

DGT deployment

Soils (800-1000 g) were spread in plastic boxes (24×30×2.5 cm), resulting in a soil depth of approximately 1 cm. Soil water contents were increased to saturation point (assessed visually) with Milli-Q water the night before deployment. DGT devices containing the MAF gels with either 0.6 mm or 1.2 mm diffusive gels were deployed on soils for 10 different deployment periods (1, 2, 4, 8, 12, 16, 20, 24, 36 and 48 h). During the period of deployment the boxes were covered with plastic film to prevent evaporation. Target elements were eluted from the MAF gel by immersion in 1 mL of 1 *M* HCl solution. After elution, 9 mL Milli-Q water was added for dilution and the concentrations of Ca, K and Mg in the eluent were then analysed by an inductively coupled plasma-optical emission spectrometer (ICP-OES, PerkinElmer, Optima 7000DV) at λ of 317.933 nm for Ca, 766.490 nm for K and 279.077 nm for Mg. Phosphorus was determined colorimetrically (Murphy and Riley 1986) by a Flow Analyser (Skalar 3000, Netherlands). For all of the above tests, three replicates were used for each treatment. The concentrations of the above elements measured by DGT ($C_{DGT}$) can be calculated by Eq. (1) (Zhang and Davison 1995; Zhang et al. 1998a):

$$C_{DGT}=M\Delta g/(\mathrm{DA}t) \quad (1)$$

where Δg is the total thickness of the diffusive gel and filter paper; *M* is measured amount of target element on the resin gel; D is the diffusion coefficient of the target element in the diffusive layer at the temperature of deployment in $cm^2\ s^{-1}$; A is the area of the effective exposure window (2.54 $cm^2$); and *t* is the deployment time.

Statistical analysis

Analysis of variance (ANOVA) was performed using GENSTAT 15$^{th}$ edition to assess whether significant difference exists between the measured $C_{DGT}$ values with deployment times and between two types of diffusive gels at each deployment time.

## Results and discussion

### Blanks and detection limits

Minimum detection limits (MDL) of Ca, K, Mg and P on the MAF gels are summarised in Table 2. The MDLs were calculated using the method described by Thompson et al. (1987). All the MDLs were lower than 5 μg device$^{-1}$. The MDL for the mass of K on the MAF gel measured using the 0.6 mm diffusive gel was 4.82 μg device$^{-1}$, which was lower than the previously reported 8.2 μg device$^{-1}$ (Zhang et al. 2013). The MDL for the mass of P on the MAF gel measured using the 0.6 mm diffusive gel was 0.04 μg device$^{-1}$, which was also much lower than the previously reported 0.15 μg device$^{-1}$ (Zhang et al. 2013).

**Table 2** Calculated blank (mean and standard deviation) and method detection limit (MDL) for Ca, K, Mg and P using the MAF gel using two different thicknesses of diffusive gel, N=5.

| Element | Thickness of diffusive gel (mm) | Blank (μg device$^{-1}$) | MDL (μg device$^{-1}$) |
|---|---|---|---|
| Ca | 0.6 | 3.24±0.14 | 4.16 |
| | 1.2 | 2.66±0.10 | 3.35 |
| K | 0.6 | 3.52±0.19 | 4.82 |
| | 1.2 | 2.15±0.19 | 3.39 |
| Mg | 0.6 | 1.73±0.23 | 3.26 |
| | 1.2 | 1.29±0.19 | 2.57 |
| P | 0.6 | 0.03±0 | 0.04 |
| | 1.2 | 0.03±0 | 0.04 |

### Potassium measurement using the DGT device

#### *Competing cation effects on K measurements*

Non-linear uptake of K by the DGT that is not attributed to supply processes from the soil system may occur in a DGT soil test when excessive amounts of competing cations are present in soil solution. The theoretical limit of generating linear K uptake by the DGT was reported to be 10.5 μeq of Ca per device, 5.7 μeq of Mg per device or 15.5 μeq of mass total (Ca+K+Mg) per device (Zhang et al. 2014). Potassium uptake was assumed to be affected due to excessive accumulation of Ca on the MAF gel (as indicated by significant differences

in $C_{DGT}$ values with diffusive gel thickness) from 48 h (0.6 mm) for soil CN, 8 h (0.6 and 1.2 mm) for soil IN, 20 h (0.6 mm) and 36 h (1.2 mm) for soil KY (shown as square symbols in Fig. 1). For soil NK, K uptake by the MAF gel was not affected by the competing ions up to 48 h deployment using either 0.6 or 1.2 mm diffusive gels. For soil GA, $C_{DGT}$ values were below the MDL due to low K concentrations in the soil. Potassium uptake by the MAF gel for soil KY was restricted as a function of excessive amounts of competing cations in soil solution. However, K uptake by the MAF gel for soil IN was restricted more than that in soil KY. Higher $C_{DGT}$ values for Ca for soil IN explain the extent of K uptake restrictions by cations (Fig. 2). Conversely, higher exchangeable Ca was observed for soil KY (15379 mg $kg^{-1}$) than soil IN (2286 mg $kg^{-1}$). Therefore, the available pools of Ca and Mg extracted by DGT are not equal to the exchangeable pools extracted by traditional procedures, which is in agreement with the poor correlation relationship of DGT-measured Ca and Mg and exchangeable Ca and Mg reported by Zhang et al. (Zhang et al. 2014). However, to avoid the effect of competing cations on K uptake by the MAF gel in soils, a deployment time of less than 8 h should be considered for some soils, considering the competing effects after 8 h on soil IN.

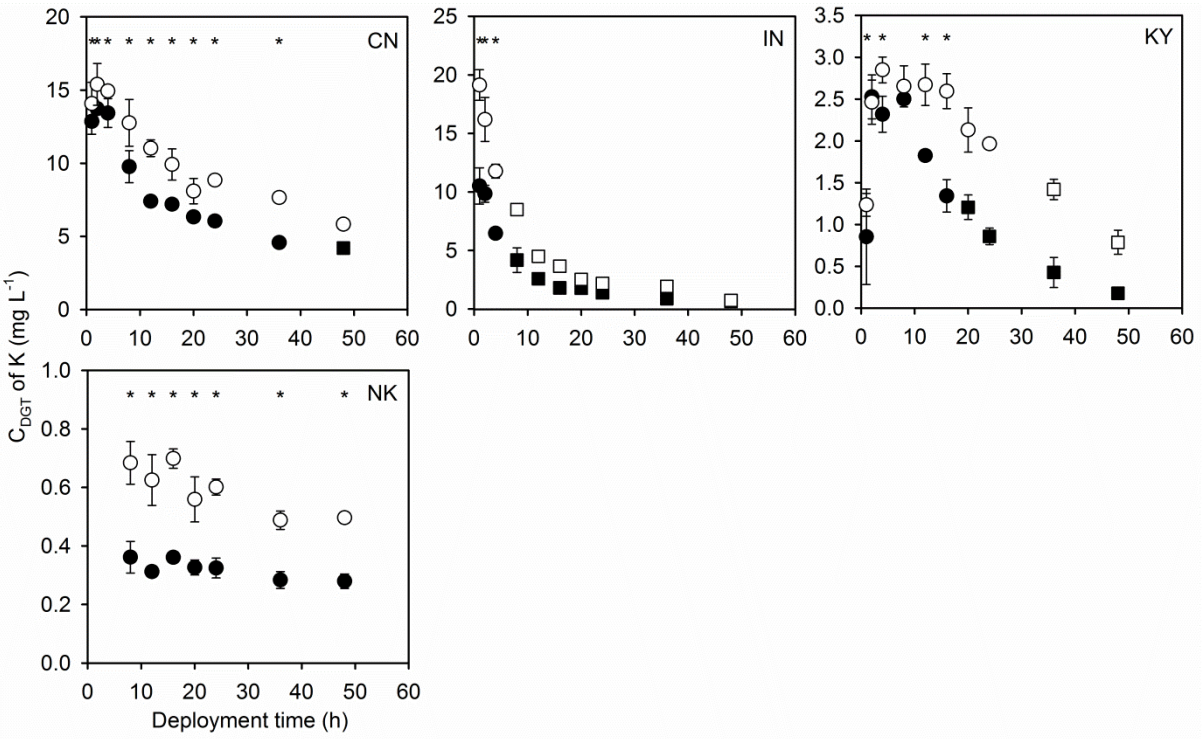


**Fig. 1** Measured values of $C_{DGT}$ for K in soils for different deployment times using 0.6 mm (●) and 1.2 mm (○) diffusive gels, where the square symbols mean that K uptake by the MAF gel is affected by excessive amounts of Ca and/or Mg indicated by the theoretical mass limit; error bars represent standard errors of three replicates; * means significant difference of $C_{DGT}$ values obtained by using 0.6 mm and 1.2 mm diffusive gels at $P \leq 0.05$ for each deployment time, while NS means no significance in general.

*Effects of deployment time on $C_{DGT}$ values for K*

Measurements of $C_{DGT}$ values for K at different deployment times demonstrated different K resupply regimes in these soils (Table 3). The measured $C_{DGT}$ values in soils CN, IN (1.2 mm diffusive gel only) and KY changed significantly with deployment time. The measured $C_{DGT}$ of K increased over short deployment times ~1-2 h for CN and then decreased with longer deployment times, irrespective of the thickness of the diffusive gels. A similar pattern of results over time was also observed for KY using a 0.6 mm diffusive gel. There was a significant increase of $C_{DGT}$ of K from 1 to 2 h deployment for KY using 1.2 mm diffusive gel, no difference found between 2 to 16 h deployment (LSD=0.64 mg $L^{-1}$) and then a decrease of $C_{DGT}$ with longer deployment times. The measured $C_{DGT}$ values for K in soil NK was not significantly affected by deployment times using 0.6 and 1.2 mm diffusive gels

(P≤0.05). As soil NK contains 96% sand (Table 1), it can be inferred that K in soil solution in these sandy soils can diffuse longer distances compared to the clay soils, resulting in a larger effective depth sampled by the DGT device in soils with higher sand content. Conversely, shorter effective distance of K diffusion to the DGT surface in soils with higher clay content also explains the relatively poor K resupply ability of soils CN, IN and KY. As the exchangeable K and KBA in NK were lower than that in other soils (except the KBA of CN), it appears exchangeable K content and KBA are not necessarily related to K resupply ability of a soil to the DGT surface.

**Table 3** Significance of effects (P values) of time on $C_{DGT}$ values for Ca, K, Mg and P; the number in brackets indicates the LSD value.

| Soil | Diffusive gel thickness (mm) | Ca | K | Mg | P |
|---|---|---|---|---|---|
| CN | 0.6 | <0.001 (3.53) | <0.001 (1.84) | 0.003 (0.47) | 0.343 |
| | 1.2 | <0.001 (4.05) | <0.001 (2.83) | 0.866 | 0.412 |
| GA | 0.6 | <0.001 (3.51) | - | <0.001 (1.73) | - |
| | 1.2 | 0.265 | - | 0.598 | - |
| IN | 0.6 | <0.001 (14.89) | 0.060 | <0.001 (2.19) | 0.075 |
| | 1.2 | <0.001 (14.99) | 0.024 (4.72) | <0.001 (1.47) | 0.222 |
| KY | 0.6 | <0.001 (5.58) | 0.006 (0.87) | 0.196 | <0.001 (10.68) |
| | 1.2 | <0.001 (4.56) | 0.002 (0.64) | 0.002 (1.44) | 0.030 (7.42) |
| NK | 0.6 | 0.007 (0.57) | 0.382 | - | - |
| | 1.2 | 0.089 | 0.062 | - | - |

"-" means the DGT values obtained for these soils were below MDL.

*Effects of the thickness of diffusive gel on $C_{DGT}$ values for K*

In general and in the absence of effects of competing cations, higher $C_{DGT}$ values for K were observed for all soils when the thicker diffusive gel was employed (Fig. 1), which is in agreement with a previous study examining the relationship of $C_{DGT}$ values for Cd, Cu and Pb and thickness of diffusive gels in the presence of humic acid in the solution (Gaabass et al.

2009). Further statistical analysis indicated the $C_{DGT}$ values for K measured using the two thicknesses of diffusive gels were significantly different at each deployment time ($P \leq 0.05$), except the 8 h deployment time for soil KY. The measured $C_{DGT}$ values for K in soil KY were more stable using the 1.2 mm diffusive gel from 2~16 h deployment than that using 0.6 mm diffusive gel, indicating the increased thickness of the diffusive gel lowers the flux of K to the DGT device, and consequently prolongs the time of K resupply from soil solution to the DGT surface. Subsequently there is a sharp decrease of the $C_{DGT}$ values for K with time indicating a poor resupplying process of K from the soil solid phase to soil solution due to further K depletion by the DGT device. We assume that $C_{DGT}$ values measured with a deployment time longer than the time required for $C_{DGT}$ values to peak measures K both in soil solution and partly the resupply from the soil solid phase. This is likely to be similar to the pools of soil K accessed by plant roots. Consequently $C_{DGT}$ values for K measured with a deployment time shortly after the initial peak could potentially more accurately predict plant K requirement than $C_{DGT}$ measured at shorter deployment times. Therefore, using a thicker diffusive gel reduces K flux required by the DGT device and provides more time for K to resupply from the soil solid phase to the DGT surface, potentially mimicking better plant K uptake processes and therefore increasing the chance that DGT-K can accurately measure the plant available pool of K in soils. In terms of competing cation effects, K uptake by the MAF gel could be affected earlier in theory using a 0.6 mm diffusive gel compared to a 1.2 mm diffusive gel. Therefore, a thicker diffusive gel can also avoid competing effects of K uptake by the DGT in soil KY to some extent.

Calcium measurement using the DGT device

There were significant changes in measured $C_{DGT}$ values for Ca with deployment time in soils CN, GA (0.6 mm), IN, KY and NK (0.6 mm) (Table 3), while no significant changes were found for soil GA using 1.2 mm diffusive gel and for soil NK using 1.2 mm diffusive

gel (Table 3). The measured $C_{DGT}$ values for Ca for soil IN decreased with deployment time (Fig. 2), indicating a weak Ca resupply ability from the soil solid phase. The $C_{DGT}$ values for Ca were relatively stable over time for soil CN (after 2 h), GA, KY (after 2 h) and NK. In general, the decrease in $C_{DGT}$ values for Ca with time was not as sharp as $C_{DGT}$ values for K (Fig. 1). This potentially could be attributed to a lower diffusion coefficient for Ca through the diffusive gel (the diffusion coefficient of Ca through the diffusive gel is 50% that of K (Chapter 3), resulting in a smaller flux of Ca accumulated by the DGT device. Therefore, deployment time has a smaller effect on measured $C_{DGT}$ values for Ca when deployment time is longer than 4 h.

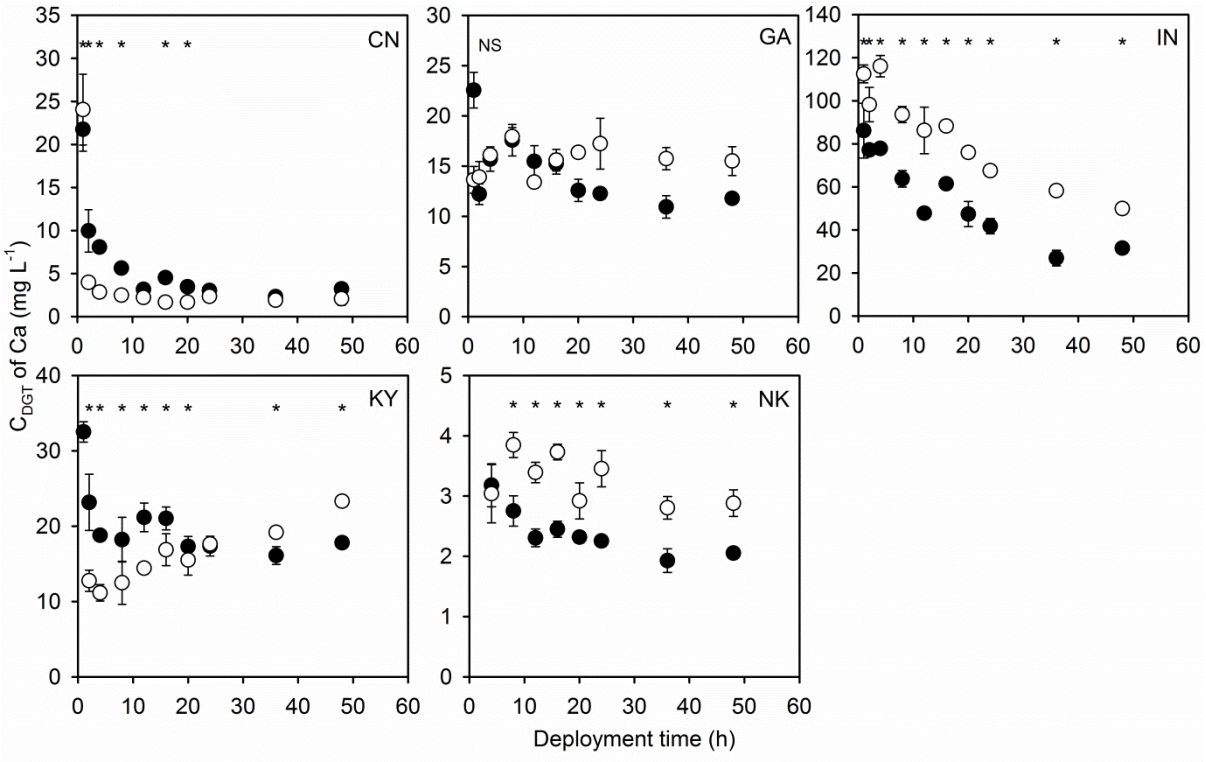


**Fig. 2** Measured values of $C_{DGT}$ for Ca in soils for different deployment times using 0.6 mm (●) and 1.2 mm (○) diffusive gels; error bars represent standard errors of three replicates; * means significant difference of $C_{DGT}$ values obtained by using 0.6 mm and 1.2 mm diffusive gels at $P \leq 0.05$ for each deployment time, while NS means no significance in general.

There was no consistent effect of diffusion gel thickness on $C_{DGT}$ values for Ca across soils. In two soils (IN and NK), generally higher $C_{DGT}$ values for Ca were observed with the thicker diffusive gels, in two soils they were lower (CN and KY) and in one soil (GA) there

was no significant difference (Fig. 2). It is not clear why lower $C_{DGT}$ values for Ca were observed for soil CN and KY at short deployment times using the 1.2 mm diffusive gels. Deployment time generally had a significant effect on $C_{DGT}$ values for Ca with the greatest changes being at short deployment times (Table 3 and Fig. 2).

Magnesium measurement using the DGT

DGT values for Mg in soil NK were below the MDL which is unsurprising given the every low concentrations of exchangeable Mg in this soil (Table 1). Effects of deployment time on $C_{DGT}$ values for Mg were similar to those for Ca (Fig. 3). There were significant changes of $C_{DGT}$ values for Mg with deployment time for CN (0.6 mm), GA (0.6 mm), IN and KY (1.2 mm) (Table 3), although the magnitude of the changes was small, especially compared to $C_{DGT}$ values for K (Fig. 1). This may have been due to the lower diffusion coefficient of Mg through the diffusive gel (47% of K - Chapter 3), resulting in a smaller flux of Mg to the DGT device. Therefore, the accumulation of Mg from soil solution is slower than that of K. The sharpest decrease with time in $C_{DGT}$ values for Mg was observed in soil IN, indicating a weak Mg resupply ability from the soil solid phase in this soil.

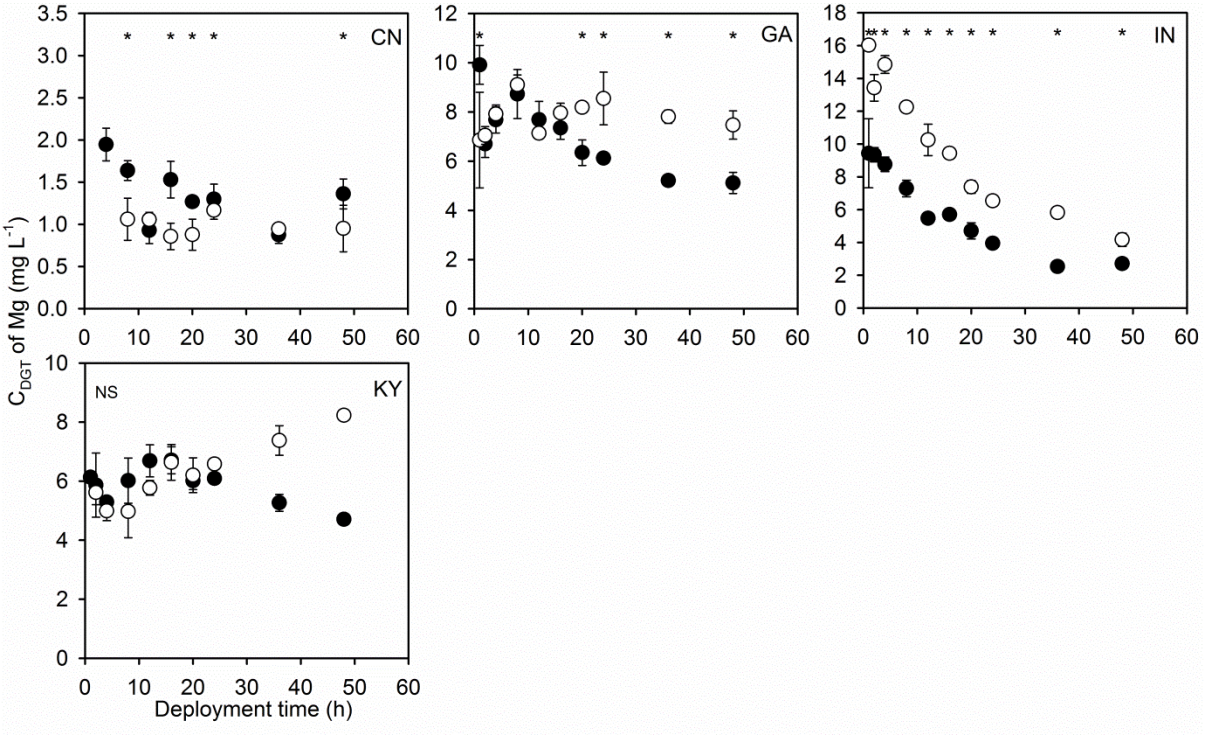


**Fig. 3** Measured values of $C_{DGT}$ for Mg in soils for different deployment times using 0.6 mm (●) and 1.2 mm (○) diffusive gels; error bars represent standard errors of three replicates; * means significant difference of $C_{DGT}$ values obtained by using 0.6 mm and 1.2 mm diffusive gels at $P \leq 0.05$ for each deployment time, while NS means no significance in general.

The similar patterns of Ca and Mg accumulation with deployment time and diffusion gel thickness indicate that the available Ca and Mg desorb and diffuse through soil similarly, perhaps related to hydrated ion radius and chemical valence (Nightingale 1959). Similar to the results for Ca, deployment time generally had a significant effect on $C_{DGT}$ values for Mg with the greatest changes being at short deployment times (Table 3 and Fig. 3).

Phosphorus measurement using the DGT

DGT values for P in soils GA and IN were below the MDL due to low P concentrations in soil solutions. Deployment time did not affect values of $C_{DGT}$ for P in soils CN and IN using either gel thickness (Table 3). Generally $C_{DGT}$ values for P using the thicker gel were more stable with deployment time compared to Ca, K and Mg (although only data for three soils are available). Like the other elements, the greatest changes in $C_{DGT}$ values for P were at

shorter deployment times. The diffusion coefficient of P through the diffusive gel is 54% of the coefficient of K at 22 $^{o}$C, resulting in a smaller flux of P accumulated by the DGT device. Consequently the rate of P uptake by the DGT device is smaller than the rate of P replenishment from the soil solid phase, resulting in stable $C_{DGT}$ values of P with deployment times in most scenarios. Data are needed for more soils to confirm that the stability with time for P is common, and if so could provide the opportunity for simultaneous measurement of K using the MAF gel. However, if $C_{DGT}$ values for P are found to commonly change rapidly at short deployment times, this is at odds with the need for shorter deployment times for determination of available K using the DGT device due to effects from competing cations (Zhang et al. 2014).

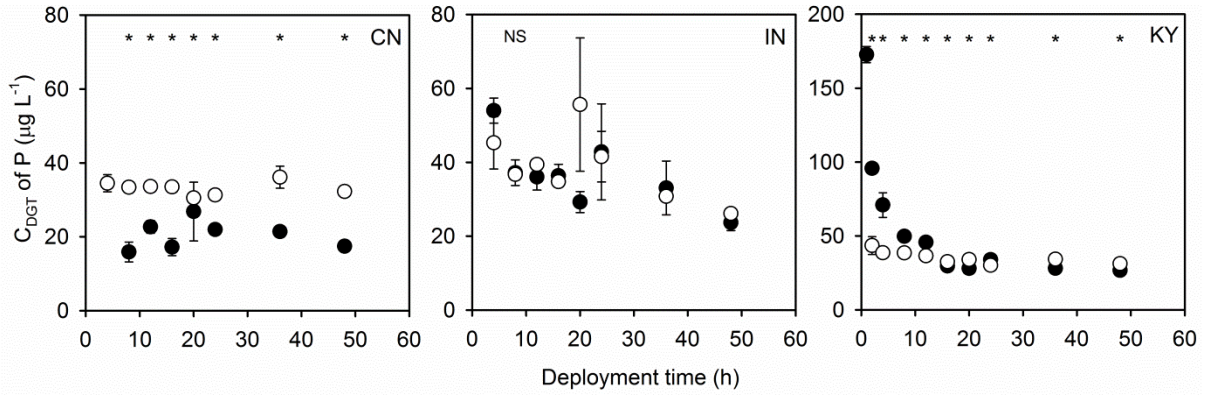


**Fig. 4** Measured values of $C_{DGT}$ for P in soils for different deployment times using 0.6 mm (●) and 1.2 mm (○) diffusive gels; error bars represent standard errors of three replicates; * means significant difference of $C_{DGT}$ values obtained by using 0.6 mm and 1.2 mm diffusive gels at P≤0.05 for each deployment time, while NS means no significance in general.

Gel thickness had significant but inconsistent effects on $C_{DGT}$ values for P in two soils (CN and KY) and no effect in soil IN (Fig. 4). The lack of effect of gel thickness in soil IN indicates P diffusion controlled the process of P accumulation by the DGT devices rather than the rate of P dissociation from the soil solid phase, which is similar to the situation for P measurement in simple solutions that have sufficient P and are stirred vigorously.

## Conclusions

The effects of deployment time on $C_{DGT}$ values for K using the MAF gel were greater than those for Ca and Mg, while there was some suggestion that P might be relatively stable. The largest effects of deployment time were generally seen at the shorter times. Thickness of the diffusive gel also affected the accumulation of all these elements, but not consistently across soils. The combined effects of the deployment time and thickness of diffusive gel on measured $C_{DGT}$ values was in the order of: K>Ca=Mg>P. There was no close relationship between the KBA of the soils and the resupply of K from the soil solid phase to soil solution measured by the DGT method. In order to apply the DGT technique to predict plant available K in soils, modified deployment times and gel thicknesses might be required in order to improve correlations between measured $C_{DGT}$ values for K and plant K uptake from soils. Future work that assesses plant growth response to addition of different rates of K rates to soil should be carried out in order to fully explore the abilities of the DGT method to predict plant available K in agricultural soils.

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# CHAPTER 5

## Prediction of wheat response to an application of potassium under different root densities in glasshouse conditions using the DGT and extraction methods

This work contained in this chapter will be submitted to Plant and Soil.

# Statement of Authorship

| | |
|---|---|
| Title of Paper | Prediction of wheat response to an application of potassium under different root densities in glasshouse conditions using the DGT and extraction methods. |
| Publication Status | ○ Published, ○ Accepted for Publication, ○ Submitted for Publication, ◉ Publication style |
| Publication Details | This chapter is prepared in publication style for the Journal of Plant and Soil. |

## Author Contributions

By signing the Statement of Authorship, each author certifies that their stated contribution to the publication is accurate and that permission is granted for the publication to be included in the candidate's thesis.

| | | | |
|---|---|---|---|
| Name of Principal Author (Candidate) | Yulin Zhang | | |
| Contribution to the Paper | Experimental development, performed analysis on all samples, data analysis and critical interpretation, wrote the manuscript. | | |
| Signature | | Date | |

| | | | |
|---|---|---|---|
| Name of Co-Author | Gunasekhar Nachimuthu | | |
| Contribution to the Paper | Experimental development, performed analysis on samples, data interpretation, reviewed the manuscript. | | |
| Signature | | Date | 28/01/2015 |

| | | | |
|---|---|---|---|
| Name of Co-Author | Sean Mason | | |
| Contribution to the Paper | Supervised development of work, data analysis and interpretation, reviewed and edited the manuscript. | | |
| Signature | | Date | |

| | | | |
|---|---|---|---|
| Name of Co-Author | Michael J. McLaughlin | | |
| Contribution to the Paper | Supervised development of work, data analysis and interpretation, reviewed and edited the manuscript. | | |
| Signature | | Date | |

| | | | |
|---|---|---|---|
| Name of Co-Author | Ann McNeill | | |
| Contribution to the Paper | Supervised development of work, data analysis and interpretation, reviewed and edited the manuscript. | | |
| Signature | | Date | |

**Abstract**

*Background and aims* An accurate soil K test would help guide K fertilizer application. The diffusive gradients in thin films (DGT) method has been shown to measure a K pool in soils different from the traditional extraction methods. The aims of this research were to 1) investigate the accuracy of predicting wheat growth and tissue K concentration under K fertilization using the DGT K method and traditional extraction methods; and 2) compare the performances of these methods under two root densities.

*Methods* Wheat (*Triticum aestivum L.,* cv. Frame) was grown in 9 typical Australian agricultural soils with 4 K rates at two root densities in a glasshouse trial for 28 days. Traditional ($CaCl_2$, Colwell and $NH_4OAc$) and DGT measurements were carried out for soils with all K rates. To assess how well the different tests predicted K responsiveness, the relative yield (= yield in control soil relative to that at optimal K supply) and wheat tissue K concentrations were plotted against the K test value of the control soil.

*Results* The yield response was generally more pronounced at high root density than at low root density. The Colwell and $NH_4OAc$ K methods had the highest accuracy for predicting wheat relative yield to K application in control soils at low root density (closest to field conditions). To obtain 90% of maximum relative yield, the critical values of the Colwell and $NH_4OAc$ K methods were 76 mg $kg^{-1}$ and 80 mg $kg^{-1}$, respectively. The $CaCl_2$ K method predicted wheat relative yield with K application fairly well at both root densities ($R^2$=0.64 for high root density and $R^2$=0.55 for low root density), while the DGT K method failed to predict wheat relative yield at low root density. The accuracy of these methods for predicting wheat tissue K concentration was in the order of DGT K > $CaCl_2$ K >>Colwell K and $NH_4OAc$ K methods.

*Conclusions* The Colwell and $NH_4OAc$ K methods were most accurate at predicting wheat relative yield compared to other methods at low root density. The DGT K method had the ability to accurately predict wheat tissue K concentrations under K application irrespective of root densities but not yield responses. Further work was needed to validate the accuracy of these methods in field conditions.

**Keywords** DGT, Diffusion, Potassium, Soil testing, Critical value

## Introduction

Potassium (K) is essential for plant growth, accounting for up to 6-10% of plant dry matter (Leigh and Wyn Jones 1984; Spear et al. 1978). As one of the major macronutrients required for plants, K is involved in many plant physiological functions, such as enhancing enzyme activity, controlling osmoregulation and cell extension and improving protein synthesis in cells (Fischer 1968; Fischer and Hsiao 1968; Marschner 1995). It is generally accepted that sufficient K status in plants lowers the risk of plant diseases and pests (Bergmann 1992; Perrenoud 1990; Prabhu et al. 2007), while insufficient K status can lead to reduced quality in crop products (Gerardeaux et al. 2010; Wong 2001) and higher populations of pests (Walter and DiFonzo 2007). Potassium has been defined as the "quality element" for crop products (Pettigrew 2000; Usherwood 1985) as it seems to play a more important role than most other nutrients in this regard. With the increasing demand for food quality, maintaining sufficient K levels in crop products becomes more important in agricultural activity.

Accurate soil testing methods for measuring "plant-available" K not only maximize agricultural product yield and quality, but also avoid long term K depletion of fertile farm lands such as those occurred in grain cropping regions of eastern Australia (Bell et al. 2010). To achieve these aims, scientists have long been studying K forms in soils and the mechanisms of K uptake by plant roots. The different (operationally defined) forms of K in soils are solution K, exchangeable K, non-exchangeable K (slowly exchangeable K) and mineral K, with K present in these pools in equilibrium with each other (Barber 1995; Huang et al. 2012). Plant available K refers to mainly soluble K and exchangeable K (McLean and Watson (1985), although some non-exchangeable K can become soluble or exchangeable during the course of a plant growing season. Plants take up K mainly from soil via roots, as K foliar application is not widely employed. It is accepted that there are 3 mechanisms of plant nutrient uptake from soils, diffusion, mass flow and root interception. Barber et al.

(1963) proposed that K reached plant roots mainly by diffusion rather than by root interception and mass flow. Subsequent work by Barber (1995) showed that K taken up by corn roots supplied by diffusion accounted for 80% of the overall total K uptake in a fertile Alfisol silt loam. Other evidence, provided by Mills et al. (1996) suggested that approximately 85% of the K moved to root surfaces by diffusion through water films around soil particles. Further, Baligar (1985) reported that diffusion contributed more to K uptake by plants than mass flow, with 99% and 96% of total K uptake occurring by diffusion for corn (20 days growth) and wheat (25 days growth), respectively. Therefore, it is apparent that plants take up mainly the soluble and exchangeable K forms from soils with most of the plant available K moving from the soil solid phase to root surfaces by diffusion. Direct contact of nutrients with plant roots can also play an important role in nutrient uptake, as increased root volume in soils provides more contact of root surface to soil. Potassium-deficient plants have reduced root to shoot dry weight ratios (Cakmak et al. 1994; Marschner et al. 1996), and indeed, Fusseder and Krauss (1986) reported that K uptake by maize in field conditions decreased from 50% to 12% when root density varied from >2 cm $cm^{-3}$ to <2 cm $cm^{-3}$. Consequently, it becomes difficult to predict plant K requirements accurately using soil testing alone as the root growth of plants is unpredictable and dependant on many other factors, such as soil bulk density, soil compaction, soil moisture, temperature and light, other nutrient supply, microorganism activity, etc.

For predicting plant growth under application of K, soil test value corresponding to 90% relative yield, the ratio of yield on non-fertilized soil to maximum yield on fertilized soil, is usually recommended calculate the most appropriate rate of K to be applied. Apart from relative yield, plant tissue concentration is also used for validating plant available K levels in soils (Bergmann 1992; Leigh and Johnston 1983). Although plant K concentration in tissue can vary with time and in different parts of the same plant (Barraclough and Leigh 1993;

Greenwood et al. 1980), K concentration of the whole plant (dry weight basis) stays at a similar at the same stage of plant growth (Greenwood and Stone 1998). The most common soil tests for predicting available soil K are soil solution extraction and chemical extraction methods. The solution K method measures K in soil solution and easily exchangeable K from the soil solid phase using water or 0.01 *M* $CaCl_2$, while chemical extraction methods attempt to measure less easily exchangeable K, using one or a combination of extractants to displace K from soils. It is well established that the $CaCl_2$ K method measures an intensity factor while the $NH_4OAc$ K (exchangeable K) method measures a quantity factor (Beckett 1964b; McLean and Watson 1985). Barber (1981) reported that K uptake is influenced more by the K quantity factor at high root density situations while K uptake is influenced more by the K intensity factor at low root density situations. Bell et al. (2009) reported that soil solution K values varied by 6-7 fold in soils having similar exchangeable K content over different soil types. It can be concluded that measures of K intensity and quantity differ greatly across soils with varying soil properties. For example, Houba et al. (1990) acknowledged that $CaCl_2$ did not extract all of the exchangeable K from soils, especially soils with high clay contents. In a glasshouse trial using Guinea grass, Darunsontaya et al. (2012) suggested that the $NH_4OAc$-K method predicted K availability more accurately than other extraction methods (water, $HNO_3$, $HNO_3$−$NH_4OAc$) and the total K method. However, Krishna (2002) reported that response of wheat to K application predicted using the exchangeable K method was soil type dependent, more specifically the K buffering ability associated with clay content. Another extraction method is the Colwell K method (extraction using $NaHCO_3$), reported to be the most widely used method for measuring available K in Australia (Rayment and Lyons 2010). However, Gourley et al. (2007) reported that pasture response to K application measured by the Colwell K method was also soil type dependent, as the critical values increased with clay content. Since neither the quantity factor nor the intensity factor appears to accurately predict

plant-available K consistently across a range of soils and crop types, a combination of the quantity-intensity (Q/I) relationship was proposed and studied to predict K availability in soils (Beckett 1964a; b; Roux and Sumner 1968; Sharma et al. 2012). For the Q/I relationship measurement, exchangeable K is proposed as the quantity factor and the ratio of K to Ca and Mg is regarded as the intensity factor. However, the Q/I relationship of K is used mainly to understand K availability of a specific soil rather than to predict plant K requirement by soil testing, due to the complicated procedures required for Q/I measurements compared to a traditional soil test.

The diffusive gradients in thin films (DGT) technique has been successfully used to more accurately predict plant available phosphorus (P) compared to traditional extraction methods (Mason et al. 2013; Mason et al. 2010; Menzies et al. 2005; Six et al. 2012; Six et al. 2014; Speirs et al. 2013; Zhang et al. 1998). The theory of element uptake by the DGT from soil samples has been extensively discussed (Ernstberger et al. 2005; Harper et al. 1998; Mason et al. 2005; Nolan et al. 2003). Simply, when a DGT device is deployed on water-saturated soil samples, the target element in soil solution diffuses through the diffusive gel and accumulates in the resin gel. When the element concentration at the DGT surface is lowered by uptake by the resin gel, the element from the soil solid phase desorbs to replenish this depletion. Therefore, the fraction of an element measured by the DGT is assumed to incorporate the soluble pool and part of the insoluble pool from the soil solid phase. Degryse et al. (2009) reported that DGT has the potential to predict plant requirement better than other extraction methods when the uptake of an element is dependent on diffusional supply to plant roots. As discussed before, diffusion contributes a large proportion of K uptake by plants. Consequently, the DGT method is likely to be more applicable than the traditional extraction methods for measurement of plant-available K in soil.

Tandy et al. (2012) proposed that the DGT method could be used for soil K measurement by using Amberlite IRP-69 as the resin gel and found a similar accuracy to the $NH_4OAc$ K method to predict K concentrations in winter barley grown in pots. However, some limitations were also reported in terms of short deployment time, limited K concentration range and difficulty caused by the curved shape of the resin gel. The Amberlite gel was assumed to be K specific and the competing effect of Ca on K uptake by the DGT devices were reported to be negligible for fertile agricultural soils (Tandy et al. 2012). Recently, Zhang et al. (2013) optimized the resin gel by using a mixed Amberlite and ferrihydrite (MAF) gel (to allow simultaneous measurement of P and K) and the MAF gel showed great advantages over the resin gel used by Tandy et al. (2012). Zhang et al. (2014) investigated the effects of competing cations on K uptake and concluded that competing cations like calcium ($Ca^{2+}$) and magnesium ($Mg^{2+}$) do restrict K uptake by the DGT, however, K uptake by the DGT was found to be linear with deployment time until a mass limit of those cations was reached. More extensive quantification of the effects of competing cations on K uptake by the DGT will facilitate assessment of the accuracy of the DGT method in predicting plant growth response to K application.

The aims of this research were to 1) investigate the accuracy of predicting wheat response to fertilizer K application (i.e. plant available K concentrations in soil) and wheat tissue K concentrations using the DGT K method along with traditional extraction methods; and 2) compare the predictive performances of these soil tests under two root densities.

## Material and methods

### Soil characterisation

Soils from typical grain producing areas across Australia with known low available K levels were dried and sieved to ≤ 2 mm. Nine soils varying in texture and other inherent soil

properties were used in the glasshouse trial (Table 1). Soil pH was measured using 0.01 *M* $CaCl_2$ solution using a soil to solution ratio of 1:5 (Rayment and Higginson 1992); organic carbon was measured using the Walkley and Black method (Rayment and Higginson 1992); exchangeable Ca, Mg and cation exchange capacity (CEC) were extracted using 1 *M* $NH_4OAc$ (Rayment and Higginson 1992); soil particle size was determined using the method described by Bowman and Hutka (2002); water holding capacity was measured using the same method as Jenkinson and Powlson (1976).

**Table 1** Basic physical and chemical properties of the soils.

| Site | Name | State | EC (μS $cm^{-1}$) | pH | Organic Carbon (%) | Clay (%) | Sand (%) | Silt (%) |
|---|---|---|---|---|---|---|---|---|
| Karoonda | KD | SA | 93 | 6.43 | 0.28 | 3 | 95 | 2 |
| Lake Bolac | LB | VIC | 90 | 5.78 | 1.33 | 3 | 92 | 4 |
| Ngarkat | NK | SA | 17 | 6.55 | 0.62 | 4 | 94 | 2 |
| Gindie B | QB | QLD | 47 | 6.95 | 0.47 | 67 | 18 | 15 |
| Capella B | QC | QLD | 48 | 7.04 | 0.60 | 68 | 20 | 12 |
| Kingaroy | QL | QLD | 59 | 5.30 | 1.11 | 41 | 43 | 16 |
| Sibson | QS | QLD | 67 | 6.01 | 0.51 | 66 | 12 | 22 |
| Regans Ford | RF | WA | 141 | 6.14 | 2.17 | 4 | 94 | 2 |
| Wickepin | WN | WA | 69 | 5.32 | 0.81 | 6 | 88 | 6 |

Glasshouse trial

A glasshouse trial was designed to investigate the effects of root density on K uptake by wheat using small and large relative soil volumes, and how this affected the relationship between soil tests and wheat response to K fertilizer. The soils were amended with nutrient solutions containing 100 mg $kg^{-1}$ of nitrogen ($NH_4NO_3$), 3 mg $kg^{-1}$ of copper ($CuSO_4•5H_2O$), 5 mg $kg^{-1}$ of magnesium ($MgSO_4•7H_2O$), 3 mg $kg^{-1}$ of manganese ($MnSO_4•H_2O$) and 10 mg $kg^{-1}$ of zinc ($ZnSO_4•7H_2O$), which altogether resulted in a total of 15 mg $kg^{-1}$ sulphur (Zhang et al. 2011). Phosphorus (as $H_3PO_4$) was applied at different rates for each soil to provide

sufficient available P for wheat plants based on PBI values and initial P status as assessed by DGT. In order to obtain a yield response curve for wheat, K (as KCl) was applied at 4 different rates (Table 3). After addition of nutrient solutions, the soils were thoroughly mixed and incubated for 2 days. The pots were sealed with plastic bags to prevent nutrient from leaching and moisture loss. Initially 500 g of each soil (3 replicates) was separated into a small pot, 1250 g of each soil (3 replicates) was separated into a large pot and 100 g was left as a subsample for soil analyses. Five pre-germinated seeds of wheat (*Triticum aestivum L.*, cv. Frame) were sown in each pot and thinned to two in the small pots and one in the large pots after one week at the two-leaf growth stage. Soil moisture was maintained at approximately 65% of the water holding capacity throughout the experiment. A randomised block design was employed and pot positions were changed randomly twice a week within the block to minimize any effects due to spatial variations in growing conditions (e.g. light, temperature and humidity) within the glasshouse. During the course of the experiment, the temperature ranged from 22 to 24 $^{o}$C, relative humidity ranged from 25 to 88 %. Wheat was harvested 28 days after sowing at mid/end tillering (GS30) (Zadoks et al. 1974). Since the root density obtained for each soil between treatments was similar (assessed visually), wheat roots were removed by washing from one replicate of each K rate, from both small pots and large pots, and dried to constant weight, resulting in 4 replicates for each soil. The dry mass was recorded to calculate root density.

## Soil analyses

### *Extraction methods*

The subsamples, separated before planting, were dried to constant weight at 40 $^{o}$C and sieved to 2 mm again for soil K testing. $CaCl_2$ K was extracted using 0.01 *M* $CaCl_2$ at a soil to solution ratio of 1:10 for 2 h (Salomon 1998); Colwell K was extracted using 0.5 *M* $NaHCO_3$ (pH 8.5) at a soil to solution ratio of 1:100 for 16 h (Colwell 1965; Rayment and Higginson

1992), and $NH_4OAc$ K was measured using 1 *M* $NH_4OAc$ at a soil to solution ratio of 1:10 for 30 min (Rayment and Higginson 1992). Potassium in the eluents from the above tests was analysed by an inductively coupled plasma-optical emission spectrometer (ICP-OES, PerkinElmer, Optima 7000DV) at λ of 766.490 nm.

*DGT methods*

A mixed Amberlite and ferrihydrite (MAF) gel was used as the binding gel for K and other cations. The MAF gel and 0.6 mm diffusive gel were prepared as described by Zhang et al. (2013). The 1.2 mm diffusive gel was prepared by using two spacers while casting the gel solution. Standard DGT devices (DGT Research Ltd, Lancaster, UK) with an effective sampling area of 2.54 $cm^2$ were used to load the gel assemblies (MAF gel, diffusive gel and filter paper). Soil samples in small containers were moistened with Milli-Q water (18.2 MΩ cm) to saturation point (assessed visually) the night before deployment. As the effects of deployment time and thickness of the diffusive gel on the measured $C_{DGT}$ of K were reported to be significant (Chapter 4), DGT devices containing either the 0.6 mm diffusive gels or 1.2 mm diffusive gels were deployed for 3 or 6 h, with temperature recorded at regular intervals during the deployment. DGT devices were rinsed with Milli-Q water to wash off extra soil particles after deployment. The MAF gels were also rinsed with Milli-Q water before being transferred to 1 mL of 1 *M* HCl for elution. Potassium in the eluent was measured by an ICP-OES after adding 9 mL of Milli-Q water for dilution. Concentrations of Ca and Mg in the eluent were simultaneously analysed at λ of 317.933 nm for Ca and 279.077 nm for Mg as these ions can compete for K on the resin (Zhang et al. 2014). The concentration of K measured by the DGT method ($C_{DGT}$) was calculated as described in previous publications (Zhang and Davison 1995; Zhang et al. 2013; 2014).

Correlations between values of soil K test methods

Correlations between the values of different soil K test methods were analysed using the Spearsman correlation method using software SigmaPlot 12.0. The soil test values were carried out on both the control soils and soils including that with K application separately.

Plant relative yield and plant K analyses

The dry weight of aboveground plant parts was recorded after drying at 60 $^{o}$C in an oven to constant weight. Maximum yield obtained for each soil was calculated by fitting a Mitscherlich curve to yields and applied K rates using Eq (1) in SigmaPlot 12.0:

$$Y_{max} = Y_0 + a\big(1 - \exp(-bx)\big) \quad (1)$$

where $Y_0$ is the wheat dry mass obtained in control soils; $a$ and $b$ are the parameters of the curve; ($Y_0$+$a$) equals the maximum yield ($Y_{max}$); relative yield at each treatment is expressed as the ratio of dry matter yield to the $Y_{max}$ obtained.

Plant tissue K concentration was analysed by the acid digestion method (McBeath et al. 2011; Zarcinas et al. 1987). Plant samples (0.5 g) were digested in 5 mL of nitric acid until the volume reduced to 1 mL, and then the solution was diluted to 20 mL for filtration. The filtered solution was then analysed by an ICP-OES as outlined above.

Comparison of different soil testing methods

The accuracy of the soil testing methods for predicting wheat relative yield and tissue K concentrations on control soils was compared by fitting the data to a Mitscherlich curve (Eq 1). The critical value of each soil test method for indicating K deficiency was determined at 90% relative yield (Holford et al. 1985; Menzies et al. 2005). While fitting the Mitscherlich curve, all yields were scaled to a relative basis by setting ($Y_0$+$a$) to 100. For the DGT K method, any treatments where competing cations could have affected the measured value for K (Zhang et al. 2014) were excluded. The critical value of each soil test method to obtain 90%

maximum tissue concentration was also determined by fitting the Mitscherlich curve. In addition, the critical values for each soil test method (where applicable) for obtaining 90% relative yield and 90% of maximum tissue concentration on all soils (including control soils and soils with K applications) were calculated in order to compare with the values for control soils.

## Results

Correlations between soil tests

A significant correlation was obtained between the Colwell K and the $NH_4OAc$ K methods ($R^2$=0.93, P<0.01, Table 2). Significant correlations ($R^2 \geq 0.95$, P<0.01) were also found between the DGT K methods. However, no significant correlation was found between either Colwell K or $NH_4OAc$ K methods with the DGT K methods. The $CaCl_2$ K method had moderate correlation with the Colwell K ($R^2$=0.49, P<0.01) and $NH_4OAc$ K methods ($R^2$=0.51, P<0.01), and correlated well with the DGT K methods ($0.76 \leq R^2 \leq 0.79$, P<0.01).

**Table 2** Spearman correlation coefficients of seven different soil K testing methods on control soils.

| | **Colwell K** | **$NH_4OAc$ K** | **DGT K 0.6 mm 3 h** | **DGT K 1.2 mm 3 h** | **DGT K 0.6 mm 6 h** | **DGT K 1.2 mm 6 h** |
|---|---|---|---|---|---|---|
| $CaCl_2$ K | 0.49* | 0.51* | 0.79* | 0.76* | 0.77* | 0.79* |
| Colwell K | | 0.93* | NS | NS | NS | NS |
| $NH_4OAc$ K | | | NS | NS | NS | NS |
| DGT K 0.6 mm 3 h | | | | 0.95* | 0.98* | 0.97* |
| DGT K 1.2 mm 3 h | | | | | 0.96* | 0.96* |
| DGT K 0.6 mm 6 h | | | | | | 0.98* |

* means significant correlation is observed while NS means no significant correlation is observed ($P \leq 0.05$).

Wheat responses to K

Contrasting root densities were obtained in small and large pots, as measured after wheat plants were harvested (Table 3). Wheat grown on some control soils showed symptoms of K deficiency, i.e. yellow tips on leaves and stunted growth, reflecting low available K contents

in those soils. Good response of wheat dry matter to K application was observed in most of the small pots (Table 3). Generally, larger responses of wheat growth to K applications were observed in small pots compared to that in large pots, except for soils NK and WN. In the large pots containing soils KD and RF, the response was unexpectedly below the controls, hence $Y_{max}$ was set at the dry mass in the control soil. In the large pots of soils LB and QS, linear responses to K were observed; $Y_{max}$ was set at the dry mass for the highest K rate. Since control soils are more applicable to what farmers are after, the response of wheat growth to K application was mainly discussed based on soil test values on control soils rather than the fertilized soils.

**Table 3** Root densities and wheat dry mass in response to K application; SD means the standard deviation and $R^2$ is the coefficient obtained by fitting the Mitscherlich curve, where "-"means no $R^2$ obtained due to: a) the response in the fertilized treatment was unexpectedly below the controls, dry mass in the control soil is taken as the $Y_{max}$ and b) a linear response was observed, dry mass in highest K rate is taken as the $Y_{max}$.

| Soil | Pot size | K rate (mg kg$^{-1}$) | | | | P (mg kg$^{-1}$) | Root density (g m$^{-3}$) | SD of root density | $Y_{control}$ (g DM pot$^{-1}$) | RY of control soils (%) | $Y_{max}$ (g DM pot$^{-1}$) | $Y_{max}$ predicted (g DM pot$^{-1}$) | $R^2$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | Control | Level 1 | Level 2 | Level 3 | | | | | | | | |
| KD | Small | 0 | 50 | 150 | 300 | 300 | 169 | 74 | 0.39 | 75 | 0.59 | 0.53 | 0.64 |
| | Large | | | | | | 18 | 4 | 0.30 | 100 | 0.30 | 0.30[a] | - |
| LB | Small | 0 | 50 | 150 | 300 | 300 | 102 | 20 | 0.34 | 83 | 0.41 | 0.41 | 0.73 |
| | Large | | | | | | 26 | 3 | 0.21 | 113 | 0.24 | 0.24[b] | - |
| NK | Small | 0 | 50 | 150 | 300 | 300 | 49 | 29 | 0.15 | 39 | 0.39 | 0.39 | 1.00 |
| | Large | | | | | | 15 | 10 | 0.11 | 41 | 0.28 | 0.27 | 0.93 |
| QB | Small | 0 | 50 | 250 | 500 | 500 | 144 | 73 | 0.28 | 38 | 0.77 | 0.73 | 0.92 |
| | Large | | | | | | 27 | 13 | 0.26 | 55 | 0.49 | 0.48 | 0.99 |
| QC | Small | 0 | 50 | 250 | 500 | 500 | 148 | 38 | 0.59 | 68 | 0.86 | 0.86 | 1.00 |
| | Large | | | | | | 30 | 8 | 0.42 | 87 | 0.50 | 0.48 | 0.74 |
| QL | Small | 0 | 50 | 150 | 300 | 300 | 187 | 57 | 0.32 | 49 | 0.75 | 0.65 | 0.79 |
| | Large | | | | | | 15 | 4 | 0.27 | 86 | 0.34 | 0.32 | 0.61 |
| QS | Small | 0 | 50 | 250 | 500 | 500 | 131 | 51 | 0.48 | 63 | 0.82 | 0.76 | 0.88 |
| | Large | | | | | | 23 | 5 | 0.43 | 84 | 0.51 | 0.51[b] | - |
| RF | Small | 0 | 50 | 150 | 300 | 300 | 179 | 84 | 0.46 | 80 | 0.58 | 0.58 | 1.00 |
| | Large | | | | | | 18 | 7 | 0.25 | 100 | 0.25 | 0.25[a] | - |
| WN | Small | 0 | 50 | 150 | 300 | 300 | 86 | 19 | 0.22 | 67 | 0.33 | 0.32 | 0.96 |
| | Large | | | | | | 19 | 5 | 0.13 | 59 | 0.24 | 0.22 | 0.92 |

Performance of soil tests to predict yield response to K fertilizer

*Small pots*

The relationships between extractable K in control soils using the different methods and the relative yield response of wheat to K fertilizer are shown in Fig. 1. The Colwell K and $NH_4OAc$ K methods were poor predictors of response to K. Moderate relationships of wheat relative yield to extractable K values were obtained for the $CaCl_2$ K method in small pots ($R^2$=0.64), and for the DGT K methods ($0.56 \leq R^2 \leq 0.59$). The critical concentrations for different soil K test methods in control soils and all the soils were shown in Table 4.

**Fig. 1.** Relationship of extractable K (in unfertilized soil) with relative yield response of wheat to K fertilizer (open symbol represents the relative yield obtained from small pots and close symbol represents the relative yield obtained from large pots; the square symbols represent soils with clay content >50%).

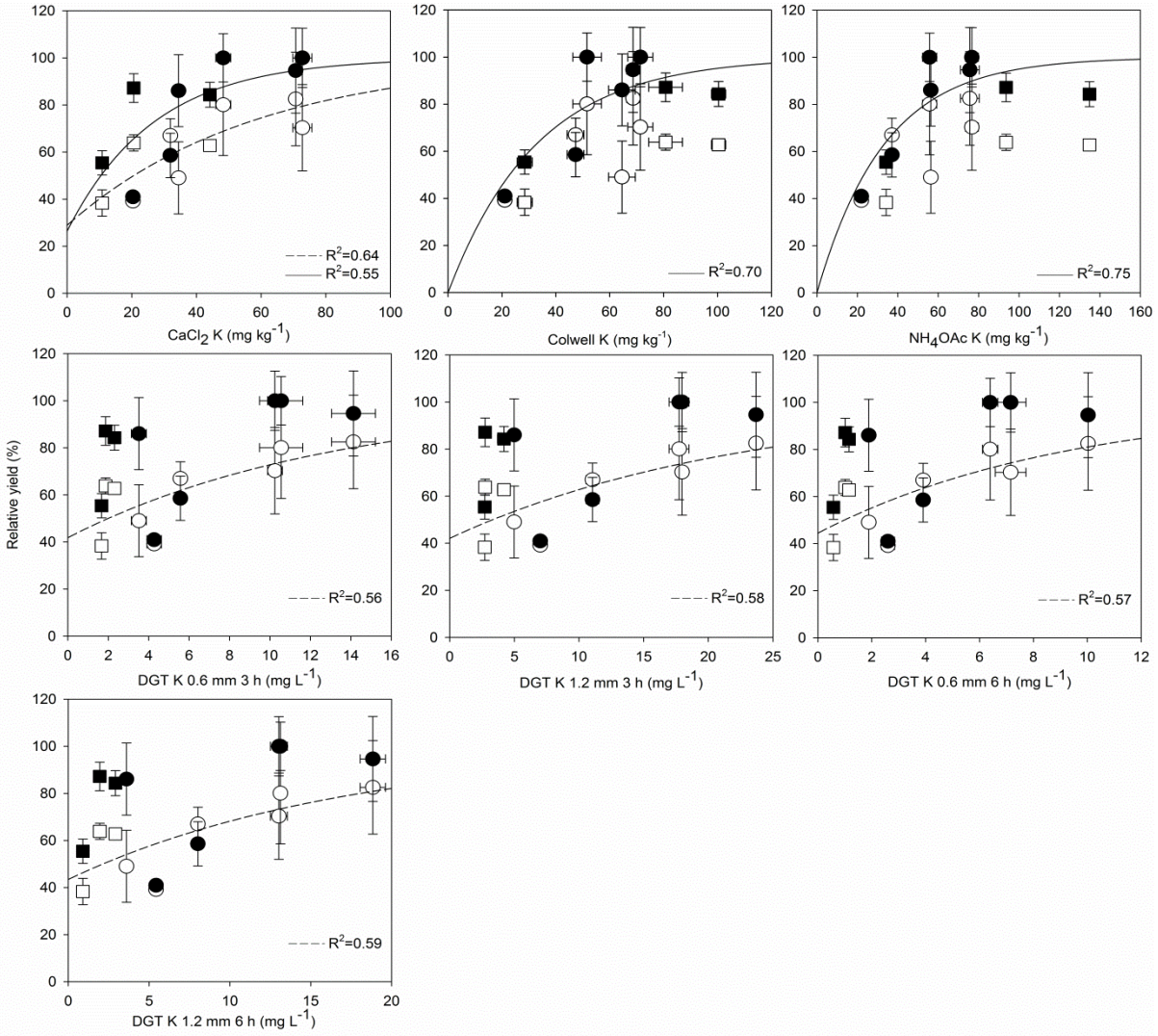


**Table 4** Critical values and correlation coefficients for each test method for obtaining 90% of maximum relative yield at two root densities; "–" means no significant relationship is observed.

| Soil test | | $CaCl_2$ K | Colwell K | $NH_4OAc$ K | DGT K 0.6 mm 3 h | DGT K 1.2 mm 3 h | DGT K 0.6 mm 6 h | DGT K 1.2 mm 6 h |
|---|---|---|---|---|---|---|---|---|
| | | | mg $kg^{-1}$ | | | | mg $L^{-1}$ | |
| *Control soils* | | | | | | | | |
| High root density | Critical value | 115 | - | - | 23 | 40 | 16 | 30 |
| | $R^2$ | 0.64 | - | - | 0.56 | 0.58 | 0.57 | 0.59 |
| Low root density | Critical value | 54 | 76 | 80 | - | - | - | - |
| | $R^2$ | 0.55 | 0.70 | 0.77 | - | - | - | - |
| *Soils with all K rates* | | | | | | | | |
| High root density | Critical value | 83 | 151 | 142 | | | 10 | 17 |
| | $R^2$ | 0.73 | 0.53 | 0.52 | | | 0.59 | 0.51 |
| Low root density | Critical value | 53 | 101 | 82 | | | - | - |
| | $R^2$ | 0.48 | 0.42 | 0.71 | | | - | - |

*Large pots*

Good relationships of wheat relative yield to measured soil K were obtained for the Colwell K ($R^2$=0.70) and $NH_4OAc$ K ($R^2$=0.75) methods in the large pots (Fig. 1). The correlation of relative yield with the $CaCl_2$ K method was moderate ($R^2$=0.55). The critical soil testing values for the Colwell K and $NH_4OAc$ K methods in control soils were 76 and 80 mg $kg^{-1}$, respectively (Table 4), with 54 mg $kg^{-1}$ for the $CaCl_2$ K method. The DGT K methods performed poorly and did not predict wheat responses to K addition.

Performance of soil tests to predict K concentrations in plants

The DGT K methods were able to predict plant K concentrations in control soils well in all pots ($R^2 \geq 0.84$) (Fig. 2). Good correlations were also found for the $CaCl_2$ K method in both small ($R^2$=0.74) and large pots ($R^2$=0.82). However, there were no correlation between the plant K concentrations in plants and the amounts of soil K extracted by the Colwell K and $NH_4OAc$ K methods. The critical tissue concentration values to reach 90% of maximum wheat tissue K concentration for the DGT K methods in the control soils varied from 12 to

53 mg $L^{-1}$ in the small pots and 3 to 9 mg $L^{-1}$ in the large pots (Table 5). The critical values for the $CaCl_2$ K method were 216 and 49 mg $kg^{-1}$ in the small and large pots, respectively.

**Fig. 2.** Relationship of extractable K with concentrations of K in wheat shoots in unfertilized soils (open symbol represents the tissue K concentrations obtained from small pots and close symbol represents tissue K concentrations obtained from large pots; the square symbols represent soils with clay content >50%).

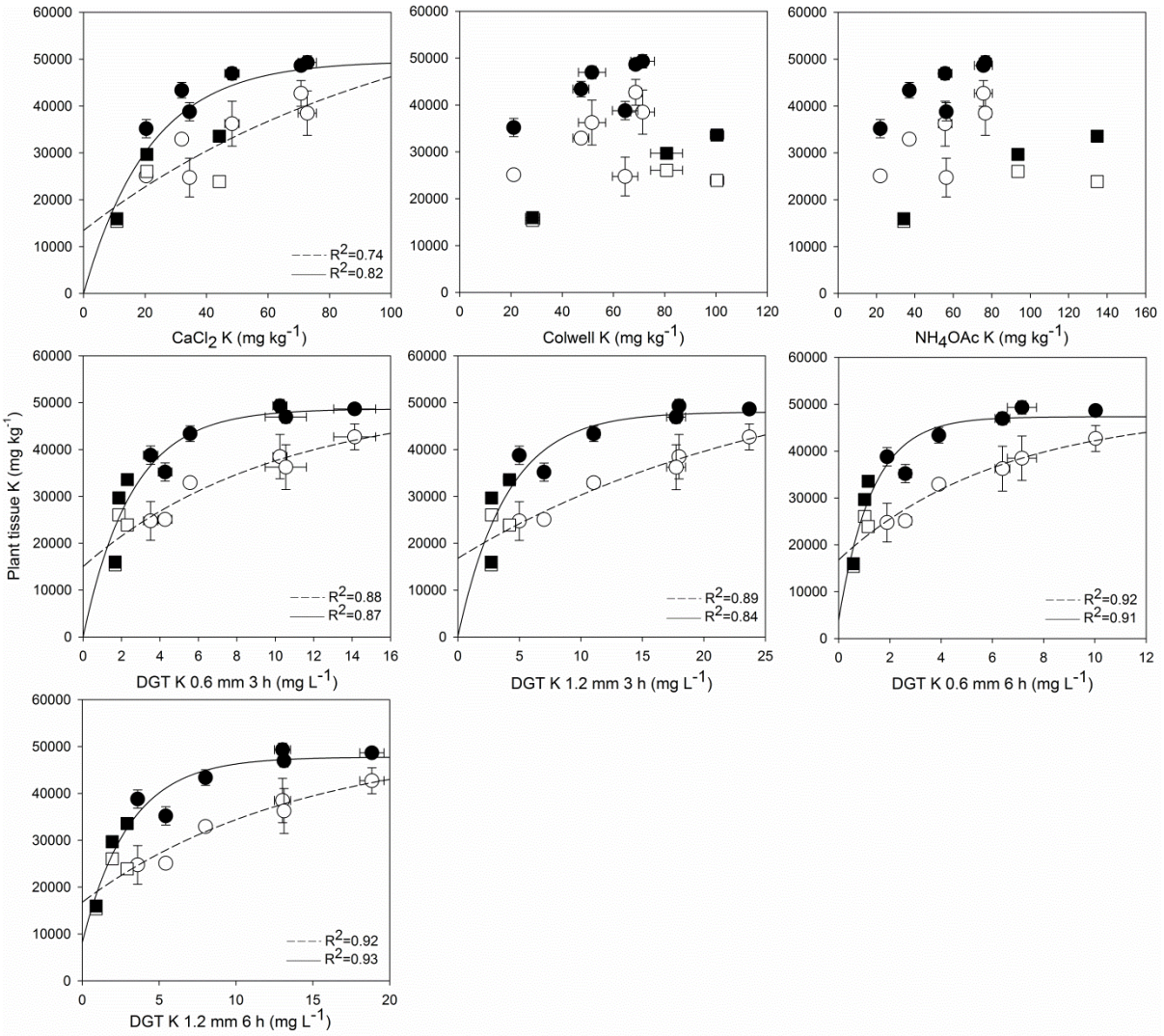


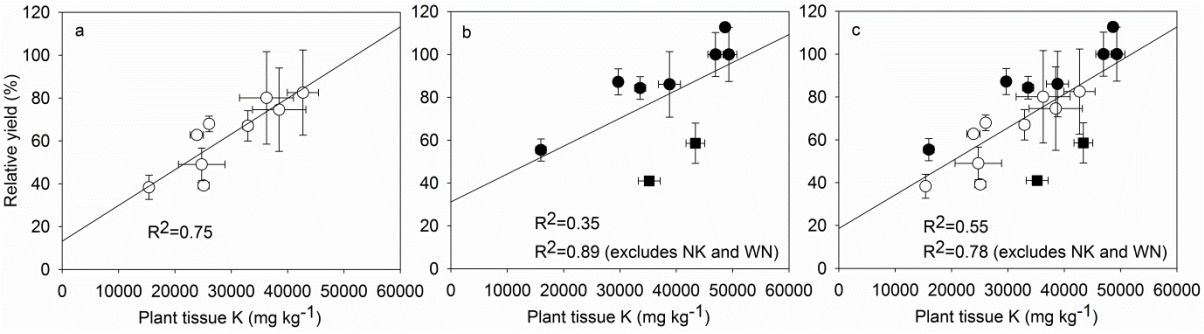
**Table 5** Tested critical value and correlation coefficient of each method for obtaining 90% of maximum K concentration in plant shoots at two root densities; "–" means no significant relationship is observed.

| Soil test | | $CaCl_2$ K | Colwell K | $NH_4OAc$ K | DGT K 0.6 mm 3 h | DGT K 1.2 mm 3 h | DGT K 0.6 mm 6 h | DGT K 1.2 mm 6 h |
|---|---|---|---|---|---|---|---|---|
| | | mg $kg^{-1}$ | | | mg $L^{-1}$ | | | |
| *Control soils* | | | | | | | | |
| High root density | Critical value | 216 | - | - | 19 | 53 | 12 | 27 |
| | $R^2$ | 0.74 | - | - | 0.88 | 0.89 | 0.92 | 0.92 |
| Low root density | Critical value | 49 | - | - | 6 | 9 | 3 | 6 |
| | $R^2$ | 0.82 | - | - | 0.87 | 0.84 | 0.91 | 0.93 |
| *Soils with all K rates* | | | | | | | | |
| High root density | Critical value | 91 | 173 | 178 | | | 11 | 15 |
| | $R^2$ | 0.79 | 0.68 | 0.54 | | | 0.77 | 0.59 |
| Low root density | Critical value | 50 | 87 | 101 | | | 3 | 4 |
| | $R^2$ | 0.83 | 0.64 | 0.34 | | | 0.76 | 0.76 |

Relationship between K concentrations in shoots and relative yield

A moderate correlation between wheat relative yields and tissue K concentrations was observed in the small pots ($R^2$=0.75, Fig. 3 a). To obtain 90% relative yield the critical tissue concentration was 45200 mg $kg^{-1}$ for the plants in the small pots. Soils NK and WN seemed to behave differently under the different root densities and the only two soils where responses to K were larger in the low root densities. The correlation coefficient was improved from 0.35 to 0.89 when soils NK and WN were excluded from the results in the large pots (Fig. 3 b). The overall critical tissue concentration to obtain 90% relative yield was 34500 mg $kg^{-1}$ for the plants in the large pots. Combing data from both pot sizes produced a single relationship with a correlation coefficient of 0.55.

**Fig. 3.** Relationships between concentrations of K in wheat shoots and relative yields of the control soils: a) small pots (open symbol), b) large pots (close symbol) and c) all pots.




## Discussion

### Correlations between soil tests

Based on the correlations for the soil K testing methods, they can be categorized into 3 groups: 1) $CaCl_2$ K method, 2) exchangeable K methods (Colwell K and $NH_4OAc$ K) and 3) DGT K methods. A high correlation between the Colwell K and $NH_4OAc$ K methods (slop of $NH_4OAc$ K/Colwell K=1.3, $R^2$=0.93, P<0.01) suggests that these two methods measure the similar K pools (quantity factor) in soils, with slightly more K extracted by the $NH_4OAc$ K than the Colwell K method. The moderate correlations between the DGT K methods and the $CaCl_2$ K method ($0.76 \leq R^2 \leq 0.79$) (and a lack of correlation between the DGT K methods with the Colwell K and $NH_4OAc$ K methods) suggests that the DGT and $CaCl_2$ methods measure similar pools of soil K (intensity factor), which is in agreement with Zhang et al. (2014). High correlations between the DGT K methods indicate that the same pool of soil K was extracted despite different gel thicknesses and deployment times. The main reason that amounts of K extracted at the 3 h and 6 h deployment times were highly correlated indicates that K flux through the DGT diffusive layer was similar. There is also the likelihood that the thickness difference of the diffusive gels employed in the DGT K tests is not large enough to produce a significant change in K resupply from soil solid phase to soil solution.

Performance of soil tests to predict yield and tissue K concentrations

To accurately guide farmers on fertilization rate to optimize crop yield, critical value obtained in non-fertilized soils, rather than nutrient cultivated soils, is more realistic to actual soil sampling procedures which occurs prior to fertilization. Since the wheat roots were constricted in the pots in the glasshouse trial and a net-like root was observed at the bottom of the pots, particularly for the small pots, we assume that the root density in the large pot was more close to the field conditions than that in the small pots. The current study showed good correlations of wheat relative yield to the Colwell and $NH_4OAc$ K methods. The critical value (90% relative yield) for the Colwell K method was 76 mg $kg^{-1}$ and the critical value for the $NH_4OAc$ K method was 80 mg $kg^{-1}$ at low root density (large pots) in the control soils. The Colwell K critical value is slightly higher that the critical value range of 40-64 mg $kg^{-1}$ for Colwell K reported by Brennan and Bell (2013) for grain yield of wheat in field conditions. Difference between critical values found in this study and the field could be attributed to differences of plant growth stage, root density, water content and subsoil K assessment for roots in field conditions. Therefore, the exchangeable K (Colwell K and $NH_4OAc$ K) methods were recommended to be better than other methods for predicting wheat growth. The study also showed moderate consistent correlations of wheat relative yield to the $CaCl_2$ K method ($R^2$=0.64 at high root density and $R^2$=0.55 at low root density) using the control soils, while a relatively good correlation was only observed at either high or low root density for other soil K testing methods (Table 4). Whilst better correlations ($0.62 \leq R^2 \leq 0.88$) were observed between the relative yield and soil testing values for the DGT K methods in the large pots without soils NK and WN, the underlying mechanisms of the overall poor performance of DGT in the large pots are not clear.

The accuracy of these methods for predicting plant tissue concentrations is in the order of: DGT K>$CaCl_2$ K>>Colwell K and $NH_4OAc$ K methods (Fig. 2). High accuracy of the DGT

K methods ($R^2 \geq 0.84$) for predicting wheat K concentrations, irrespective of root densities, suggests that DGT is an improved predictor of plant tissue K concentrations compared to other methods. The maximum K concentration in wheat tissue predicted by each method (except the Colwell K and $NH_4OAc$ K methods) were between 40000 to 50000 mg $kg^{-1}$, which is in agreement with the reported adequate K concentration in winter wheat of 35000-55000 mg $kg^{-1}$ by Bergmann (1992). To achieve 90% of relative yield, the measured plant tissue K concentrations (45200 mg $kg^{-1}$ at high root density and 34500 mg $kg^{-1}$ at low root density) were also in agreement with Bergmann's result (1992). The critical values of the DGT K methods for wheat to obtain 90% of maximum tissue concentration were between 12 and 53 mg $L^{-1}$ at high root density and between 3 to 9 mg $L^{-1}$ at low root density. When predicting wheat tissue K concentration using the DGT K methods, soils NK and WN appear to have less effect on the predicted relationships by the DGT methods. Poor prediction of wheat K concentration by the Colwell K and $NH_4OAc$ K methods appears due, for the most part, to the heavier clay soils (clay content >50%, as shown in square symbols in Fig. 2). It can be concluded that higher exchangeable K in soils does not necessarily mean a higher K concentration in plant tissue, but may indicate the potential to maintain available K in soils for plants in the following seasons.

Effects of root density on critical values for soil tests

The performance of the soil tests to predict response to K fertilizer was affected by the different root densities induced by varying pot size. The critical value increased with increased root density ($CaCl_2$ K method for control soils and soils with all K rates, Colwell K and $NH_4OAc$ methods for soils with all K rates, Table 4). The reason is presumably that higher root density creates a stronger demand on soil K pools thereby requiring a higher critical value in most soils to satisfy this demand. This indicates that calibrating soil tests with crop fertilizer requirements for K is difficult under glasshouse conditions as root

densities are higher than in the field, so that critical values determined under glasshouse conditions may not be accurate for predicting responses in the field. These inaccuracies will increase as pot size decreases. We hypothesised that at low rooting density it was more likely that intensity measures of soil K ($CaCl_2$ and DGT) might correlate well with plant response to K fertilizer, while at high root density (small pots) the capacity measures (Colwell K and $NH_4OAc$ methods) would correlate better with plant response due to significant K depletion. However, this was not the case and the intensity measures tended to perform better (in terms of explaining plant response to K fertilizer) at high root density and quantity measures (Colwell K and $NH_4OAc$ K methods) performed better at low root densities (Table 4).

Plant K concentration relationship with relative yield

Moderate correlations between wheat relative yield and tissue K concentration were observed across the control soils (Fig. 3). The correlation relationship deteriorated when values from soils NK and WN were included in the analysis. A comparison of the correlations for the control soils to that obtained for all soils (including soils with K application) showed lower correlations ($R^2$=0.58 for high root density, $R^2$=0.26 for low root density, $R^2$=0.43 for high and low root densities combined). The lowered correlation is presumably due to more points from soils NK and WN were included.

**Conclusions**

This study investigated four soil test methods to predict wheat response to K application in 9 agricultural soils in a glasshouse trial under two root densities. The predictive accuracy of soil K testing methods varied with root density. Comparing the plant growing conditions to that in the field, the low root density of plant roots in large pots was more appropriate. Therefore, the Colwell and $NH_4OAc$ K methods had the highest accuracy for predicting wheat relative yield to K application in control soils. The critical vales for 90% wheat

relative yield at mid/end tillering (GS30) stage for the Colwell and $NH_4OAc$ K methods were 76 and 80 mg $kg^{-1}$, respectively. The DGT K methods proved to be the most accurate for predicting wheat tissue K concentrations at both root densities, but they failed to accurately predict wheat relative yield responses to K applications. Assessing soil tests on their ability to predict plant K concentrations will not select the most useful test to predict response to fertilizer K addition (which is the main aim of soil K testing), and assessment of soil tests using plant growth studies in the glasshouse is markedly affected by artificially high root densities in small pots. Further study is needed to validate the performance of these soil K test methods in field conditions.

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# CHAPTER 6

## Utilization of a potassium buffering ability (KBA) measure as an indicator of potential K supply in deficient scenarios across a range of soil types

This chapter will be submitted to Plant and Soil.

# Statement of Authorship

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**Abstract**

*Background and aims* One common problem with current soil K test methods is that the critical soil test value is soil-type dependent associated with varying K binding ability of soils. In order to accurate predict plant K uptake by soil test, it is necessary to understand the relationship between the strength of K extraction by soil tests, K binding by soil solid phase and K uptake ability by plant roots.

*Methods* Potassium buffering ability (KBA) was measured by an addition of 1280 mg $kg^{-1}$ K (generated from PBI test) to nine agricultural soils, expressed as mg K loss per kilogram soil. Soil available K was also measured using the $CaCl_2$, Colwell, $NH_4OAc$ and DGT K methods after addition of different K rates. After wheat growth for 28 days, wheat K uptake was measured.

*Results* Good correlations were found between KBA and the increments of measured soil K test values under K application by the $CaCl_2$ K ($R^2$=0.95) and DGT K ($R^2$=0.96) methods. On the control soils, K removed from soils between sowing and harvest measured by the $CaCl_2$ K method was less than what wheat actually removed for most soils. A highly significant correlation ($R^2$=0.989) was found between the K removed ratio (soil:plant) with KBA.

*Conclusions* KBA could be an important indicator aiding a soil K test method as it represents the ability of soils to resupply K and therefore soil susceptibility to K deficiency in the future.

**Keywords** DGT, Potassium, Soil testing, Potassium buffering ability

## Introduction

In the previous glasshouse trial (Chapter 5), the accuracy of predicting wheat response to K application using different soil K testing methods under different root densities was assessed. The Colwell and $NH_4OAc$ methods were found to be the most accurate soil K test methods for predicting wheat relative yield at low root density which was more close to the root density typically found in the field. However, in regards to predicting responses to applications of K, the DGT K method appeared to be dependent on soil type. As reported previously, plant response to K application predicted by the Colwell and $NH_4OAc$ methods was also to be soil type dependent in some circumstances (Barber 1995; Gourley et al. 2007; Krishna 2002). The main reason of causing the soil type dependent problem was assumed to be that the Colwell and the $NH_4OAc$ methods extract more K than what plant can take up from soils with higher clay content. Therefore, K buffering ability closely relating to clay content must be taken into account in order to precisely predict plant response to K application by a soil test.

Phosphorus buffering capacity (PBC) is defined as the increase/decrease of P amount per unit soil in P solution, which reflects the ability of soils for retaining P in the soil solid phase. Phosphorus buffering indices (PBI) as a single point addition of P was proven to be closely related to PBC and to be an effective index to predict PBC of soils (Burkitt et al. 2002). Moody (2007) showed that the PBI was useful for adjusting critical values of the Colwell P method for several crops. While measuring PBI, $KH_2PO_4$ solution is used to provide an addition of P (1000 mg $kg^{-1}$) to the soil, also resulting in K addition (1280 mg $kg^{-1}$) at the same time. Therefore, soil potassium buffering ability (KBA) using the same procedure as the PBI measurement can possibly be utilized to help understand soil K dynamics.

The aims of this study were 1) to assess the influence of KBA on increases in soil test values with increasing applications of K; 2) to assess the response of various soil types to KBA when the soil solution K pool is depleted upon plant K uptake.

## Material and methods

Potassium buffering ability (KBA)

The KBA was assessed on the same nine soils utilized in the previous chapter (Table 1, Chapter 5), which were initially identified to have low concentrations of K in soil solutions. KBA was assessed using the same procedure as that to determine PBI as the salt used in the addition of 100 mg $L^{-1}$ of P is $KH_2PO_4$ and therefore an addition of 128 mg $L^{-1}$ K also occurs. Two grams of soil was mixed with 20 mL solution containing 100 mg $L^{-1}$ P, 128 mg $L^{-1}$ K in 0.01 *M* $CaCl_2$ in 50 mL tube resulting in an application of 1000 mg $kg^{-1}$ P and 1280 mg $kg^{-1}$ K. After shaking for 17 h, the K concentration in solution from an aliquot was analysed by an inductively coupled plasma-optical emission spectrometer (ICP-OES, PerkinElmer, Optima 7000DV) at λ of 766.490 nm. KBA indicating the ability of the soil to remove the applied K from solution was expressed as amount of K sorbed (mg $kg^{-1}$) by simply calculating the difference between the amount of K added with that remaining in solution after the shaking period with the soil.

Increases in soil test K values with applications of K in respect to KBA

Nine soils were treated with 3 different application rates of K (as KCl) and mixed thoroughly before 2 days incubation (see previous chapter for more details). Subsamples (100 g) of the soils were then dried to constant weight in oven at 40 $^{o}$C. Different soil K testing methods were used to measure soil K in all soils. $CaCl_2$ K was extracted using 0.01 *M* $CaCl_2$ at a soil to solution ratio of 1:10 for 2 h (Salomon 1998); Colwell K was extracted using 0.5 *M* $NaHCO_3$ (pH 8.5) at a soil to solution ratio of 1:100 for 16 h (Colwell 1965; Rayment and

Higginson 1992), and $NH_4OAc$ K was performed using 1 *M* $NH_4OAc$ at a soil to solution ratio of 1:10 for 30 min (Rayment and Higginson 1992). The DGT K method used was as described by Zhang et al. (2014), using a 0.6 mm diffusive gel and a deployment time of 6 h. Potassium in the extraction solutions was analysed by an ICP-OES as outlined previously. The increment of the soil testing value per unit of K application was plotted against KBA for each individual soil to investigate the relationship between the soil K buffering ability and the pools of applied K measured by the different soil testing methods.

Response of different soil types to K depletion as assessed by KBA

Soil response to the removal of K through plant uptake was assessed by measuring concentrations of K extracted by $CaCl_2$ only on the control soils both before and after wheat growth for 28 days. Only data from the small pots (high root density) were utilized as it was predicted that this system would have the larger impact on K removal and therefore any soil response would be easier to assess. Pre-harvest analysis has been described previously (see Chapter 5) and post-harvest analysis was performed by taking 4 cores from the full pot depth in each soil. Sampled soils were dried prior to analysis. The amounts of K removed from the soil by the wheat plants were calculated by measuring tissue K concentrations (Chapter 5) and multiplying by the yield obtained in each pot.

**Results and discussion**

Effect of KBA on increases in soil K test values with K application

A negative KBA value for soil LB indicated that some available $K^+$ moved from soil solid phase to the $KH_2PO_4$-$CaCl_2$ solution due to the weak binding ability of soil solid phase for K and a relatively high K concentration in soil solution (Table 2). To some extent, the measured KBA values are dependent on the extent of K deficiency in the soils, but the KBA is more related to the inherent properties of soils which affect K sorption. A good linear relationship

between soil clay content and the KBA values ($R^2$=0.96) confirmed that the KBA values on the selected soils can reflect the ability of soil to absorb K and the effect of the original K status in the soils associated with K levels on KBA was negligible. However, the relationship needs to be validated on a wider range of soils with varying clay mineralogy. Concentrations of K extracted by the $CaCl_2$ K, Colwell K, exchangeable K ($NH_4OAc$ K) and DGT K methods all had good linear relationships ($R^2 \geq 0.87$) with the rates of applied K for each soil type (Table 2). The slopes obtained by the $CaCl_2$ K, Colwell K and Exchangeable methods were close to 1 on soils with low clay content (<50%), except 0.65 on soil QL which had a moderate clay content (Table 2). Higher slopes obtained by the Colwell K and exchangeable methods for soils QB, QC and QL (clay content >50%) compared to that obtained by the $CaCl_2$ K method indicate that fertilizer K is more strongly retained in the exchangeable phase for these soils. The DGT and $CaCl_2$ methods were unable to measure as much of the applied K on the high clay content soils, as they reflect measures of K intensity, particularly the DGT K method as the measured increment in K extracted per mg $kg^{-1}$ K added soil was very small.

The relationships between the increase in soil K testing values with KBA are shown in Fig. 1. The best fitted correlation of increment per unit of K applied were found for $CaCl_2$ K ($R^2$=0.95) and DGT K ($R^2$=0.96) methods, as these methods only extract soil solution K and potentially weakly bound K. The exponential decay of measured increments in DGT K per K unit of application with KBA demonstrates that DGT K is very sensitive to changes in KBA and closely reflects the binding strength of K to the soil (similar to a Freundlich-shape sorption curve). The more aggressive Colwell K and $NH_4OAc$ K methods extract a large proportion of sorbed K and hence do not reflect this change in K binding strength between soil types. This may explain why the critical value for Colwell K for predicting pasture 90% relative yield is soil type dependent as reported by Gourley et al. (2007). Conversely, the K demand by the DGT device is from the diffusive gradient established in the diffusive gel,

which is dependent on the concentration gradient rather than the chemical properties of the extraction methods.

**Table 2** Basic properties of the soils used in the glasshouse trial, measured potassium buffering ability (KBA) and slope of soil test value against applied K rate in each soil; values in brackets represent the $R^2$; "a" means the DGT K value from the last K rate was not included due to competing cations, "b" means the DGT K values from the last two K rates were not included due to competing cations.

| Site | Name | State | EC (µS $cm^{-1}$) | pH | Organic Carbon (%) | Clay (%) | KBA (mg $kg^{-1}$) | Slope | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | | $CaCl_2$ K | Cowell K | $NH_4OAc$ K | DGT K (mg $L^{-1}$ per mg $kg^{-1}$) |
| Karoonda | KD | SA | 93 | 6.43 | 0.28 | 3 | 28 | 1.07 (1.00) | 0.99 (1.00) | 1.09 (1.00) | 0.11 (0.99)[a] |
| Lake Bolac | LB | VIC | 90 | 5.78 | 1.33 | 3 | -8 | 0.93 (0.98) | 0.92 (1.00) | 0.92 (1.00) | 0.12 (1.00)[a] |
| Ngarkat | NK | SA | 17 | 6.55 | 0.62 | 4 | 31 | 1.12 (0.99) | 1.07 (0.99) | 0.92 (1.00) | 0.14 (1.00) |
| Gindie B | QB | QLD | 47 | 6.95 | 0.47 | 67 | 704 | 0.41 (1.00) | 0.66 (0.98) | 0.90 (1.00) | 0.01 (1.00)[b] |
| Capella B | QC | QLD | 48 | 7.04 | 0.60 | 68 | 827 | 0.28 (1.00) | 0.60 (0.95) | 0.79 (1.00) | <0.01 (1.00)[b] |
| Kingaroy | QL | QLD | 59 | 5.30 | 1.11 | 41 | 305 | 0.65 (1.00) | 0.95 (1.00) | 0.84 (1.00) | 0.03 (0.99) |
| Sibson | QS | QLD | 67 | 6.01 | 0.51 | 66 | 610 | 0.39 (1.00) | 0.44 (0.87) | 0.78 (0.99) | 0.01 (1.00)[b] |
| Regans Ford | RF | WA | 141 | 6.14 | 2.17 | 4 | 34 | 0.92 (1.00) | 0.96 (0.98) | 1.01 (1.00) | 0.11 (1.00)[a] |
| Wickepin | WN | WA | 69 | 5.32 | 0.81 | 6 | 49 | 0.97 (1.00) | 0.91 (0.99) | 0.94 (1.00) | 0.13 (1.00) |

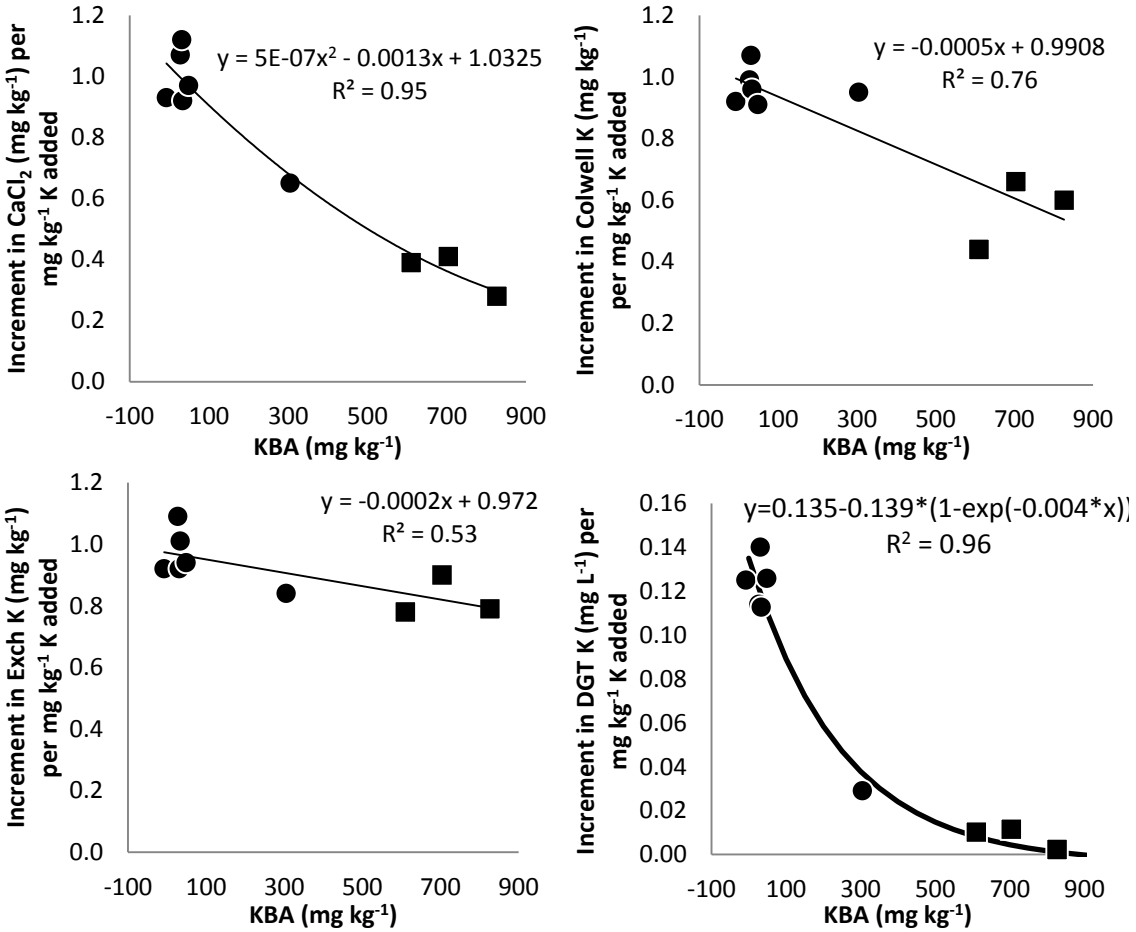


**Fig. 1.** Relationship of increment in measured soil K testing values as a function of K application and soil KBA; square symbols represent soils with high clay content >50%.

Relationship between plant K uptake and soil K loss

Due to the unrealistic high final soil solution K on soil QS, the data from soil QS were not discussed in this section. Reductions in the amount of K in soil solution between sowing and harvest as measured by the $CaCl_2$ K method (K intensity measure) did not necessarily correlate with the amount that was removed by the plants (Fig. 2). It appears that there are a group of soils that have seen very little reduction in soil solution K values even when considerable amounts of K that has been removed by the plant. These soils correspond to soils that have considerable clay content and corresponding high KBA values. When available K pools are not sufficient to supply enough K to the plant, resupply potential from other less labile sources becomes important. High ratios (close to 1) of the reduction of K as

measured by the $CaCl_2$ method to the K plant uptake from the soil indicate that the available K measured by soil test simulates the plant available fraction (Fig 3). Lower ratios suggest that plants have taken up more K than the K that was initially measured by the soil solution method. This represents scenarios where soil solution measure is relatively weak in extracting K compared to that of the plant roots. The highly significant relationship between the ratio of K removed (soil:plant) with KBA ($R^2$=0.989, Fig. 3) indicates that the KBA can be a precise soil property to predict potential changes to soil solution K values in response to sources of K removed by the plant. In general, soils with higher KBA values have a greater ability to resupply the soil solution K pool from other K pools in soil that have comparably similar levels of deficiency as measured by actual plant response (RY%) (Chapter 5).

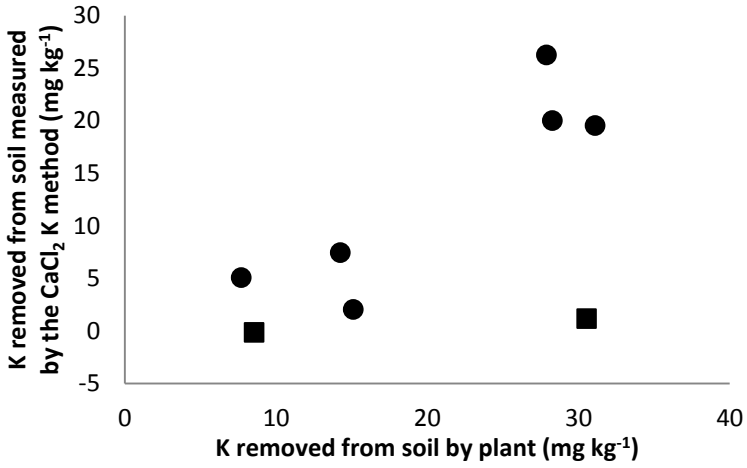


**Fig. 2.** Relationship of K removed from soil measured by the $CaCl_2$ K method and K removed by plants; square symbols represent soils with high clay content >50%.

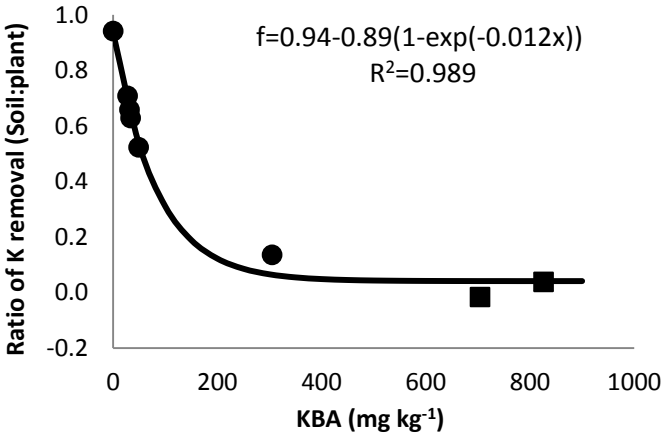


**Fig. 3.** Relationship of the ratio of K removed from soil measured by the $CaCl_2$ K method before and after plant growth to shoot K uptake and soil KBA; square symbols represent soils with high clay content >50%.

## Conclusions

The strength of extraction of K by the $CaCl_2$ and DGT methods correlates well with the KBA on soils potentially deficient in K. Compared to the Colwell K and $NH_4OAc$ K methods, the fraction of K measured by the $CaCl_2$ K and DGT K methods was more closely related to K in soil solution. Assessment of soil KBA could be an important indicator for soils that are potentially prone to decreasing available K levels and susceptibility to deficiency as they have a reduced ability to resupply soil solution K pools in response to K removal by plant roots. Therefore, it is wise to consider several soil properties together in order to attempt to predict K requirement by plants, rather than using a soil testing method alone.

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# CHAPTER 7

## Conclusions and future research

**Executive summary**

The diffusive gradients in thin films (DGT) method has been modified by producing a mixed Amberlite and ferrihydrite (MAF) gel for K measurement in soils. The MAF gel allows simultaneous measurement of Ca, K, Mg and P using the DGT technology. Since the DGT method has the ability to measure Ca, K and Mg, it is potentially a useful research tool to investigate the interactions between the major cations in soils, as well as in water and sediments. The effects of competing cations on K uptake by the MAF gel were investigated by DGT deployment on model solutions and on agricultural soils. Calcium was found to be the main competing cation prevalent in agricultural soils that affected K uptake by the MAF gel, but the competing effects can potentially be avoided by using a shorter deployment time. The deployment time was found to significantly affect the measured $C_{DGT}$ values for K. The thickness of the diffusive gel also had an effect on the measured $C_{DGT}$ values for K, but the effects were different across soils. A comparison of methods found that the Colwell K and $NH_4OAc$ K methods were better than the $CaCl_2$ K and DGT K methods for predicting wheat relative yield response to K application under glasshouse conditions at a low root density (more relevant to field conditions). Indeed, the prediction of relative yield by the DGT K method was poor and appeared to be sensitive to root density and was soil-type dependent. Yet, in the same glasshouse trial, the DGT K method showed great accuracy for predicting wheat tissue K concentrations, irrespective of root densities. Therefore, this suggests that caution is required when attempting to correlate plant tissue K concentration with expected plant response to K applications.

**Other considerations that may impact soil K testing**

A soil testing method that can be used before seeding to accurately predict K requirement by plants would be invaluable for farmers to help them manage their fertilizer application and to ensure maximum yields are obtained. To achieve this aim, substantial progress has been

made by researchers in terms of assessing K forms in soils that relate to plant requirements, mechanisms of plant K uptake and different soil K testing methods for better predicting plant K requirements. However, to accurately predict plant growth response to applied K in soils by soil testing, other factors are inevitably affecting the measured values. Soil sampling technique is the very first step that will potentially affect the applicability of the final soil testing result. The depth of soil profile to be sampled should match the average depth where most of the roots of a specific plant are distributed. Root growth also has a close relationship with nutrient availability in soils. When plant growth is limited by insufficient available nutrients, poor root growth in turn limits nutrient uptake. Wissuwa (2005) reported that larger root to shoot ratios under P deficiency enables plants to explore a greater volume of soil by increasing total root length density and root fineness. Root exudates also help release K from the soil solid phase so that it is more available for plant uptake. Rengel and Damon (2008) reported that amino acids from root exudates of wheat and sugar beet enhanced K release from clay soils. However, overall root growth is difficult to predict before seeding, as many other factors contribute to root growth such as soil type variations, individual plant species, seasonal conditions, human activities, sub soil constraints, etc.

The substitution of sodium (Na) for K in some circumstances also contributes to an inaccurate prediction of plant K requirement through soil testing. Sodium has been defined as a “functional element” and reported as having an ability to reduce the use of other essential elements by plants, due to partial substitution (Subbarao et al. 2003). Recently, Pi et al. (2014) found that in sugar beet, uptake of Na was able to substitute low K availability to a large extent in terms of plant functions although it cannot fulfil all of the fundamental roles involving K. The interactions of Na and K for wheat are relatively unknown but any substitution that occurs will cause difficulties in terms of developing accurate soil K tests.

**Role of soil K testing in management of soil K reserves**

Taking into account the above considerations and the results from this study, it appears that it may be difficult to predict K requirements by plants accurately when using a single soil K test performed at the start of the plant life cycle. However, pre-season soil testing for K remains valuable as a guide to K nutrition as it is hard to correct K deficiency once it becomes apparent in-season, due to the relatively immobile nature of K in soil. It is still important to optimize soil testing results by taking into account the main practical factors mentioned above while predicting plant K requirement.

The solution K (intensity factor) and exchangeable K (quantity factor) methods (Beckett 1964; McLean and Watson 1985) are the most common soil testing methods extensively used to predict plant K requirements. In theory, the K fraction extracted by the $CaCl_2$ K method (intensity factor) contains the available K forms in soil solution and a small portion of K from the exchangeable form; the K fraction extracted by the exchangeable K method (quantity factor) contains most of the K bound on soil exchangeable sites and the solution K. The K fractions in soils measured by the solution K and exchangeable K methods were correlated to plant tissue concentrations (Fig. 2, Chapter 5). We observed that plants in some clay-rich soils had lower tissue K concentrations while having relatively high exchangeable K values from soil tests. Soils with less clay content are prone to K deficiency due to a rapid decline in available K following crop removal, and a potassium buffering ability (KBA) value could potentially be used to help identify soils susceptible to such declines. It can be concluded that plants can take up K easier from soils with smaller KBA values due to less binding force for $K^+$ on the soil solid phase and a greater diffusion of $K^+$ towards plant roots. Therefore, we speculated that use of the intensity factor for prediction of available K is more relevant to plant K uptake for the current season, whereas the quantity factor is more relevant

in predicting available K for plant K uptake over the subsequent seasons. To efficiently manage soil available K reserves, the following measures are suggested:

Firstly, the intensity factor should be used for predicting plant K requirement for the short term (current season), while the quantity factor should be used for predicting plant K requirement for a longer term (at least more than one season), especially for soils with higher clay content. Secondly, with lower clay contents in soils, the frequency of soil testing must be increased to ensure sufficient available K in soils. Thirdly, application of K fertilizers should be modified according to the KBA of soils. Due to the different KBA of soils, it is prudent to apply higher than predicted rates of K fertilizer to soils with low KBA, while maintaining lower rates for the high buffering ability soils. Murrell (2013) suggested that no application of K in soils with low indigenous supply limits plant yield but not in soils with high indigenous supply. However, continued withdrawal of K from soils could eventually result in depletion of soil K to yield-limiting levels. For repeated crop growth cycles, the total and exchangeable K ratio could be used to predict soil K supply over time Rayment (2013). Finally, besides prediction for soil K status, plant tissue K concentration can be used as an approximate indicator of available K status in soils. Soil available K levels can also be monitored using a simple strip trial, where K fertilizer is applied in the field in a strip adjacent to a part of the field where no K fertiliser is applied to see if there is difference of crop growth (assessed visually) caused by K fertilization.

**Future research**

Considering some of the issues highlighted by the work completed in this study, and in order to optimize K fertilization based on soil K testing, further research in the following areas is recommended.

1) Further modification and testing of the DGT method for plant-available K measurement

Although the Colwell K and $NH_4OAc$ K methods predicted the wheat relative yield response better than the DGT K and $CaCl_2$ K methods at a low root density closely reflecting the field conditions, the DGT K method had a competitive advantage in predicting wheat tissue K concentrations over the other methods. However, the failure of the DGT K method for predicting plant K requirement is presumably because the DGT cannot measure enough of the K resupply capacity of soils with higher KBA values. Therefore, potential improvements of the DGT method for predicting plant-available K should look at the following aspects: a) using an alternative diffusive gel. Since the diffusion coefficient of K through the diffusive gel controls the speed of K transferal in the diffusive gel, the dynamic K equilibrium between soil solid phase and soil solution induced by the DGT is affected; b) using a new resin gel that has a larger capacity for K binding. To eliminate the effects of competing cations and limited deployment time associated with K capacity issues, a resin gel with larger capacity and specificity for K allows DGT K measurement to be deployed for longer deployment times in order to quantify more of the K resupply; c) Correlation of DGT K and other soil K tests with different crop types. Since the mechanisms of K uptake by plants may vary between plant species, the potential of the DGT K method for accurate predicting plant-available K for other plants is unclear.

2) Potassium application recommendations based on soil K testing

It appears difficult to provide an accurate prediction for fertilizer requirements based on a single soil K test as many uncontrolled edaphic, plant and environmental factors contribute to the inaccuracy of predicting plant responses based on soil testing values. However, the traditional extraction method can be used to monitor soil available K levels

over time to give a guide on dynamic changes of plant-available K reserves in soils after cropping. Until the appearance of an accurate soil testing method which can better predict K requirement by plants, it is prudent to manage soil K according to current soil K testing methods, aided by some measurements of other important soil properties. For example, building and improving the database for main cropping areas in terms of KBA will help correct the soil testing values for predicting plant K requirement and guide further management of K fertilizer application.

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# Appendices

## Appendix 1: Attempt to release K in soils using $NaHCO_3$ as measured by a DGT K test

### 1. Introduction

In previous chapter (Fig. 1 and 2, Chapter 5), relatively lower plant tissue K concentrations were observed on soils with higher clay content (>50%), but the measured Colwell/$NH_4OAc$ K values were higher in comparison to the other soils, indicating the plant-available K measured by the Colwell/$NH_4OAc$ K methods is more than that available for plant uptake. In addition, the increase in DGT K values with K application on clay rich soils were much smaller compared to sandy soil types, resulting in the DGT K method appearing to be soil type dependent in predicting plant growth as measured by relative yield. The aim of this experiment was to determine if some of the exchangeable sources of K can be measured using the DGT method when Milli-Q water is replaced with a solution containing $NaHCO_3$ during the soil moistening process.

### 2. Material and methods

Two soils Langhorne Creek (LC) and Capella (CP) were selected for the experiment, one representative each of a clay soil and sandy soil (Table A1.1). Four treatments including Milli-Q water, 0.01 *M*, 0.05 *M* and 0.1 *M* of sodium bicarbonate ($NaHCO_3$) were used to moisten the soils before DGT deployment. The DGT devices containing the MAF gels were deployed on each soil for 6 h, with 4 replicates for each treatment. Potassium in the eluents was measured by an ICP as outlined in Chapter 4.

**Table A1.1** Basic properties of the soils used for the glasshouse trial.

| Soil | State | EC (uS cm $^{-1}$) | pH | Organic Carbon (%) | Clay (%) | Sand (%) | Silt (%) |
|---|---|---|---|---|---|---|---|
| LC | SA | 99 | 6.71 | 0.88 | 6 | 93 | 1 |
| CP | QLD | 48 | 7.02 | 0.68 | 59 | 27 | 14 |

## 3. Results

Additions of $NaHCO_3$ failed to provide an increased DGT K value in both soils, LC and CP (Fig. A1.1). With the addition of $Na^+$ in soil solution this should promote $K^+$ being exchanged from soil solid phase to soil solution. However, due to a high concentration of $Na^+$ in soil solution generated from addition of $NaHCO_3$, $Na^+$ potentially becomes a competing cation for the MAF gel for K uptake.

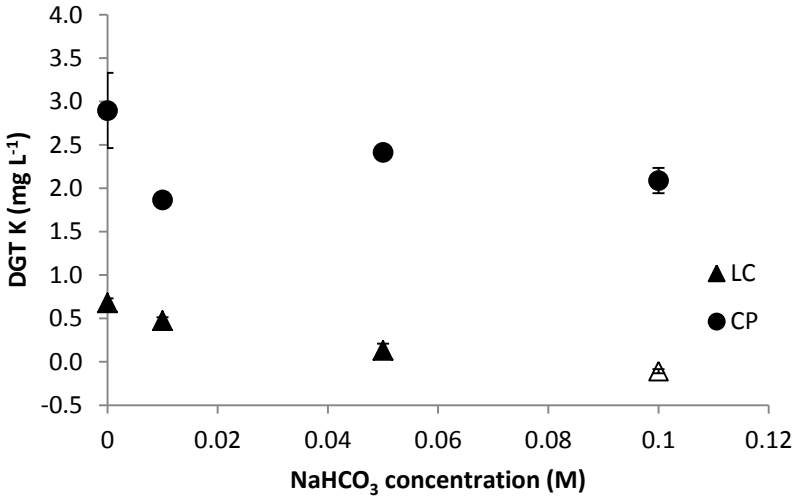


**Fig. A1.1**. Measured DGT K values in two soils moisten with water and $NaHCO_3$ solutions using the DGT methods at 6 h deployment. The open symbol represents a value that was under method detection limit.

**Appendix 2: Attempts to increase the capacity of the resin gel for K**

## 1. Introduction

In Chapter 2, $Ca^{2+}$ was reported to be the main competing cation potentially affecting K uptake by the MAF gel in Australian agricultural soils. Although, a shorter deployment time could potentially avoid the competing effects from $Ca^{2+}$, a larger capacity of the resin gel for K allows the DGT method to be used in wider deployment conditions for measuring K. Usually the absorption preference of clay for $K^+$ is higher than $Na^+$, followed by $H^+$ and $Li^+$ (Evangelou and Phillips 2005). Consequently the ion exchange between K with $H^+$/$Li^+$ is easier than that with $Na^+$. The aim of this study was to investigate if the capacity of the Amberlite based resin gel for K can be increased by replacing the $Na^+$ on the Amberlite with $H^+$ and/or $Li^+$.

## 2. Material and methods

2.1. Sodium removal by HCl

One gram of wet Amberlite (5 replicates) was mixed with10 mL of 1*M* HCl on a shaker for 30 min. the solution was separated by centrifugation (10 min, 2000 rpm). After replacing the acid with 10 mL of Milli-Q water, 1 mL aliquot of the water solution was analysed for calculating Na mass removed off the Amberlite. The process was repeated between 1 to 4 times.

2.2. Tests of the resin gels for K binding

*2.2.1. Substituting counter ions on the Amberlite with $H^+$ and/or $Li^+$.*

The Amberlite was prewashed with either LiCl or HCl solution after $Na^+$ removal off the Amberlite surface to be replaced by $Li^+$ and/or $H^+$. The prewashed process followed the above procedures. Four gel types were tested: MAF, LiCl, H+LiCl and 5HCl.

1) Normal Amberlite reagent; 2) LiCl: 2 g of wet Amberlite was immersed in 20 mL of 5 *M* LiCl. Amberlite was then washed with Milli-Q water (2 times) followed and the pH was adjusted to 7 with LiOH; 3) H+LiCl: 2 g of wet Amberlite (which was treated with 1 *M* HCl before, see above) was immersed in 20 mL of 5 *M* LiCl. Washing with Milli-Q water followed (2 times) and the pH was adjusted to 7 with LiOH; 4) 5HCl: 2 g of wet Amberlite was immersed in 20 mL of 5 *M* HCl followed by a wash with Milli-Q water (2 times) and the pH was adjusted to 7 with LiOH.

*2.2.2. Gel production*

Two grams of wet Amberlite or treated Amberlite was mixed with 1 g of wet ferrihydrite slurry to prepare the resin gel for binding K. Preparation of gels followed the same process as described for making the MAF gel in Chapter 2.

*2.2.3. Capacity test*

The above gels (4 replicates for each type of gel) were immersed in 10 mL of 200 mg $L^{-1}$ K solution (as KCl) resulting in a total amount of 2 mg K. After solution period of shaking (16 hours), K concentration remaining in the solution was measured to calculate the amount of K bound by the resin gels.

**3. Results**

3.1. Sodium removal by HCl

When HCl was used to wash the Amberlite resin, significant ($P \leq 0.05$) amounts of $Na^+$ can be replaced with $H^+$ (Fig. A2.1).

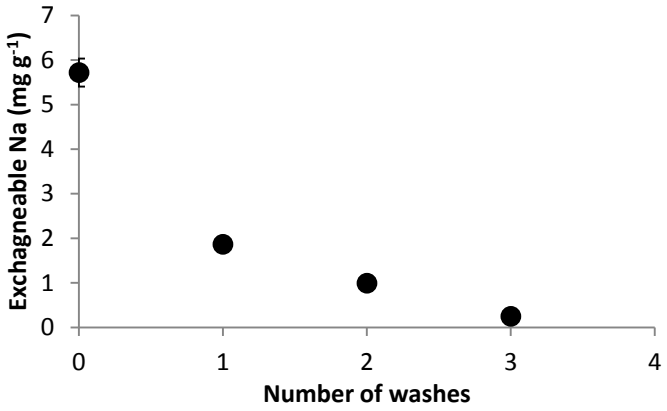


**Fig. A2.1**. Relationship of Na displaced from the Amberlite and number of washing times. LSD=0.43 mg $g^{-1}$.

3.2. Capacity for K of the treated gels

Compared to the capacity of the MAF gel, the capacity of the Amberlite based resin gel can be increased significantly ($P \leq 0.05$) by replacing $Na^+$ with $H^+$ (acid) and/or $Li^+$, (Fig. A2.2). Although the increase of the resin gel for K binding was significant, it appeared the overall benefit was relatively small for the DGT K method. Therefore, it appears not worthwhile to try and attempt to increase the gel capacity for the DGT K method.

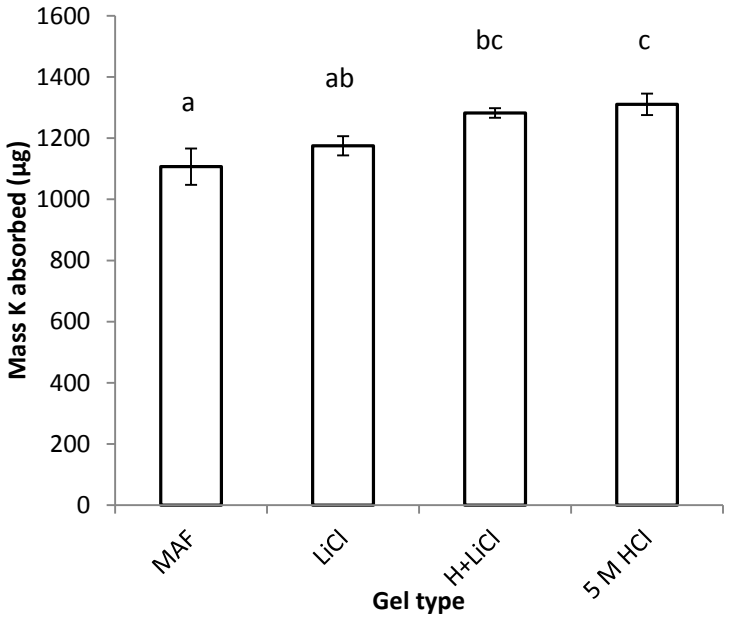


**Fig. A2.2**. K absorbed by different resin gels. Different letters mean significant difference at $P \leq 0.05$, LSD=119 µg; Error bars represent standard errors from 4 replicates.

## Appendix 3: Diffusive gel check and combined gel test

### 1. Instruction

DGT is now commercialised, consequently simplifying the procedures of the DGT test would save time and make the DGT method more competitive to other methods. The aim of this experiment is to test if a combined resin and diffusive (CRD) gel compares with the performance of using a resin gel and diffusive gel separately in a DGT test.

### 2. Material and methods

The first steps of preparing the CRD gel was the same with the MAF gel, but one of the glass plates was covered with glad wrap beforehand. After the MAF gel was settled in the oven after approximately 1 h, the glad wrap and spacer was removed and clear gel solution acting as the diffusive gel was cast on top the MAF gel with the addition of one more spacer placed in between the glass plates. Plastic DGT devices were then used to load either the gel assembly of MAF gel and diffusive gel or the CRD gel.

DGT devices containing the normal gel assembly and the CRD gels were deployed in in solution containing of 15 mg $L^{-1}$ Ca (as $CaCl_2$), 15 mg $L^{-1}$ K (as KCl and $KH_2PO_4$), 15 mg $L^{-1}$ Mg (as $MgCl_2$) and 1 mg $L^{-1}$ P ($KH_2PO_4$) for 1, 2, 4, 6, 8, 12 and 16 h, with 4 replicates for each deployment time and 5 blanks. The solution was stirred vigorously throughout the experiment. The mass of Ca, K, Mg and P were measured by an ICP as described previously in Chapter 2. The elution efficiency of the CRD gel is considered to be the same with the MAF gel. The mass was calculated using the Eq. 1:

$$M = C_{Acid\times}(10.265 + V_{dg})/0.85 \quad (1)$$

where $V_{dg}$ is the volume of diffusive gel in mL and 0.85 is the elution efficiency of the MAF gel for K.

## 3. Results

Significant differences were observed between the measured mass of Ca, K, Mg and P using the combined gels and the normal gels ($P \leq 0.05$, Fig. A3.1). For Ca, K and Mg slightly higher values obtained using CRD gels might be due to the minor contamination from the diffusive gels. Since the whole CRD gel was eluted in acid any remaining elements left in the diffusive gel part of the CRD gel might cause an overestimation of the actual mass obtained on the gel.

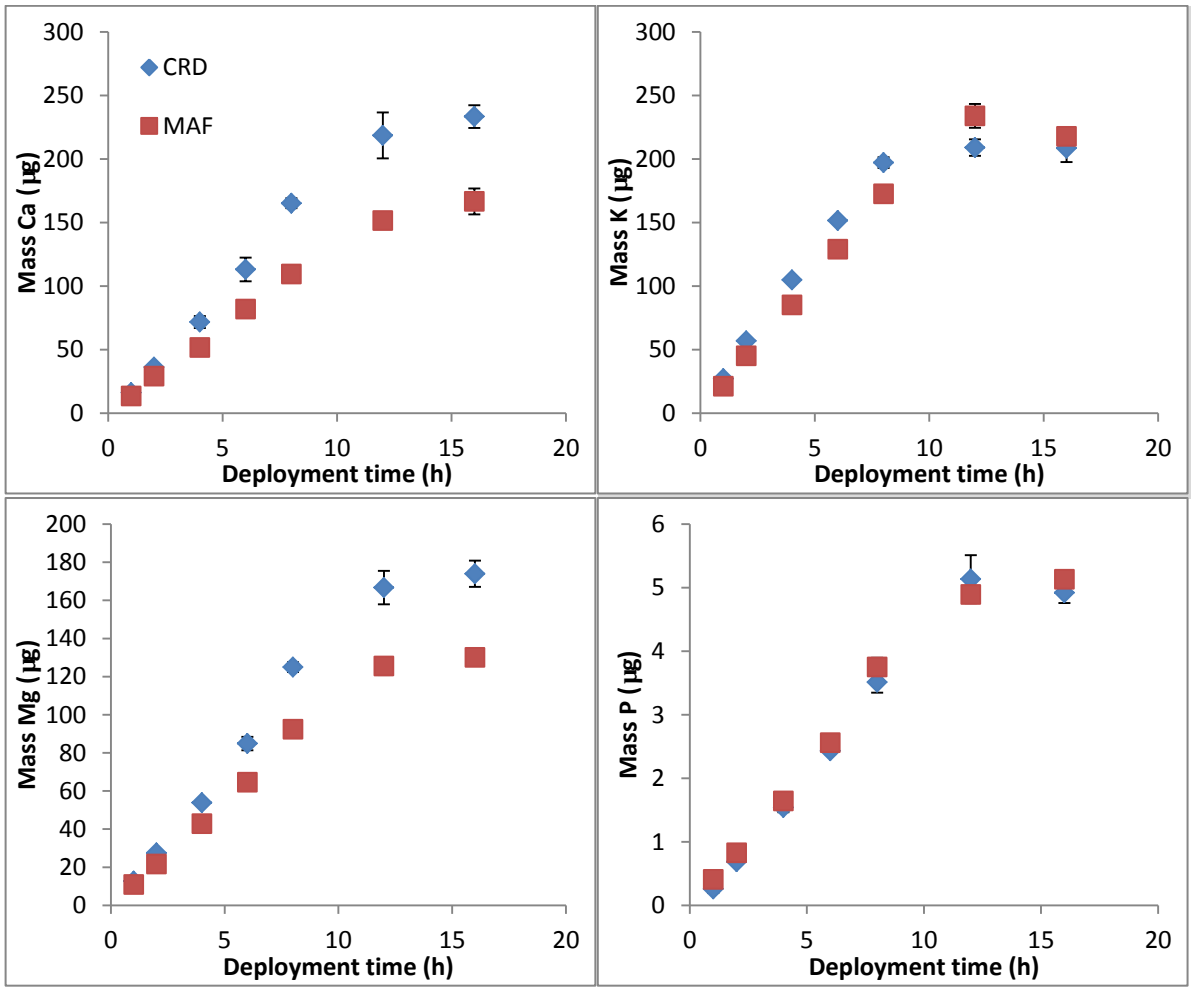


**Fig. A3.1.** Mass of element accumulated by the CRD and MAF gels, where shading means the values to be checked.

## Appendix 4: Reuse of diffusive gels in the DGT technique

### 1. Introduction

DGT as a comparative soil testing method to other extraction methods has relatively high consumables. As DGT is now commercialised for P, more emphasis has been placed on method time and cost. At this stage none of its components can be re-used, except the plastic devices. The diffusive gel acts as a matrix between the resin gel and solution outside, which theoretically has no binding ability for measured elements. Therefore, the diffusive gel is the only component that has the potential to be re-used.

### 2. Theory

On principal the measured element in a used diffusive gel after a DGT deployment should diffuse freely to clean water when the gels are washed in water. If the mass of the tested element in the diffusive gel is $M_0$ after use, the mass of element in the diffusive gel after washing n times $M_f$ can be calculated as follows:

$$M_f = M_0/(V_g + V_w)^n$$

where $V_g$ and $V_w$ are the volumes of diffusive gel and water used for washing; and n is the washing times. In theory, when $V_w \rightarrow \infty$, $M_f=0$. In practical terms, when the volume of $V_w$ is large enough and *n* is sufficient enough, $M_f$ can be negligible.

### 3. Material and methods

3.1. DGT measurements

The MAF gel was prepared according to the published procedures (Zhang et al. 2013). DGT devices containing the MAF gels were deployed on 10 agricultural soils for the traditional 24 h (3 replicates), without regard to the effect of competing ions on the practical capacity of the MAF gel for K. After deployment, the MAF gels were retrieved and placed in 1 mL of 1 *M* HCl for elution. The elution solution was diluted using 9 mL of Milli-Q water before analysis. Calcium, K and Mg in the eluent were analysed by an ICP as outlined in Chapter 2.

Phosphorus was analysed by an AutoAnalyzer. For all the above tests, three replicates were used for each treatment. The element concentration measured by the DGT was calculated by the equation below:

$C_{DGT}=M\Delta g/(DAt)$

where $C_{DGT}$ is the concentration of element measured by DGT; $M$ is measured amount of element on gel; and $t$ is the deployment time.

3.2. Diffusive gel washing and re-measurement on soils

After the first deployment, 25 used diffusive gels were washed in 1 L of Milli-Q water stirred vigorously (repeated twice), with at least 1 h between each washing. The soils were then tested again using the DGT method with the washed diffusive gels (3 replicates). Finally the DGT concentrations of the elements measured were compared using the software Genstat 15.

3.3. Diffusive gel contamination check

Gel solution, diffusive gels and MAF gels were prepared according to published procedures (Mason et al. 2005; Zhang and Davison 1995; Zhang et al. 2013). DGT devices (DGT Research Ltd, Lancaster, UK) containing the MAF gels were deployed in solution containing of 15 mg $L^{-1}$ Ca (as $CaCl_2$), 15 mg $L^{-1}$ K (as KCl and $KH_2PO_4$), 15 mg $L^{-1}$ Mg (as $MgCl_2$) and 1 mg $L^{-1}$ P ($KH_2PO_4$) for 2, 4, 8 and 16 h, with 6 replicates for each deployment time. For each deployment time, 3 diffusive gels were transferred to 1 mL of 1 M HCl for elution, and 3 were rinsed with Milli-Q water before acid elution. Finally Ca, Mg and P in the eluent from diffusive gel and MAF gels were measured.

## 4. Results

4.1. Comparison of measured $C_{DGT}$ on soils using both fresh and reused diffusive gels

Higher $C_{DGT}$ values were observed for Ca, K and Mg for the used diffusive gels in these 10 agricultural soils (Fig. A4.1), suggesting there is a certain amount of element left in the diffusive gel from previous deployments that wasn't removed with a Milli-Q rinse. The

measured $C_{DGT}$ of P for used diffusive gels were lower in most of the soils, indicating a minor difference of the $C_{DGT}$ of P obtained using the new and used diffusive gels. Although a significant difference was observed while using the used diffusive gel for Ca, Mg and P measurement in a DGT test, if the concentration in the soil or water is high, the used diffusive can still be used when higher background values are factored in. In addition, the washing method in this experiment is a dilution washing which can be improved by using a rinsing method.

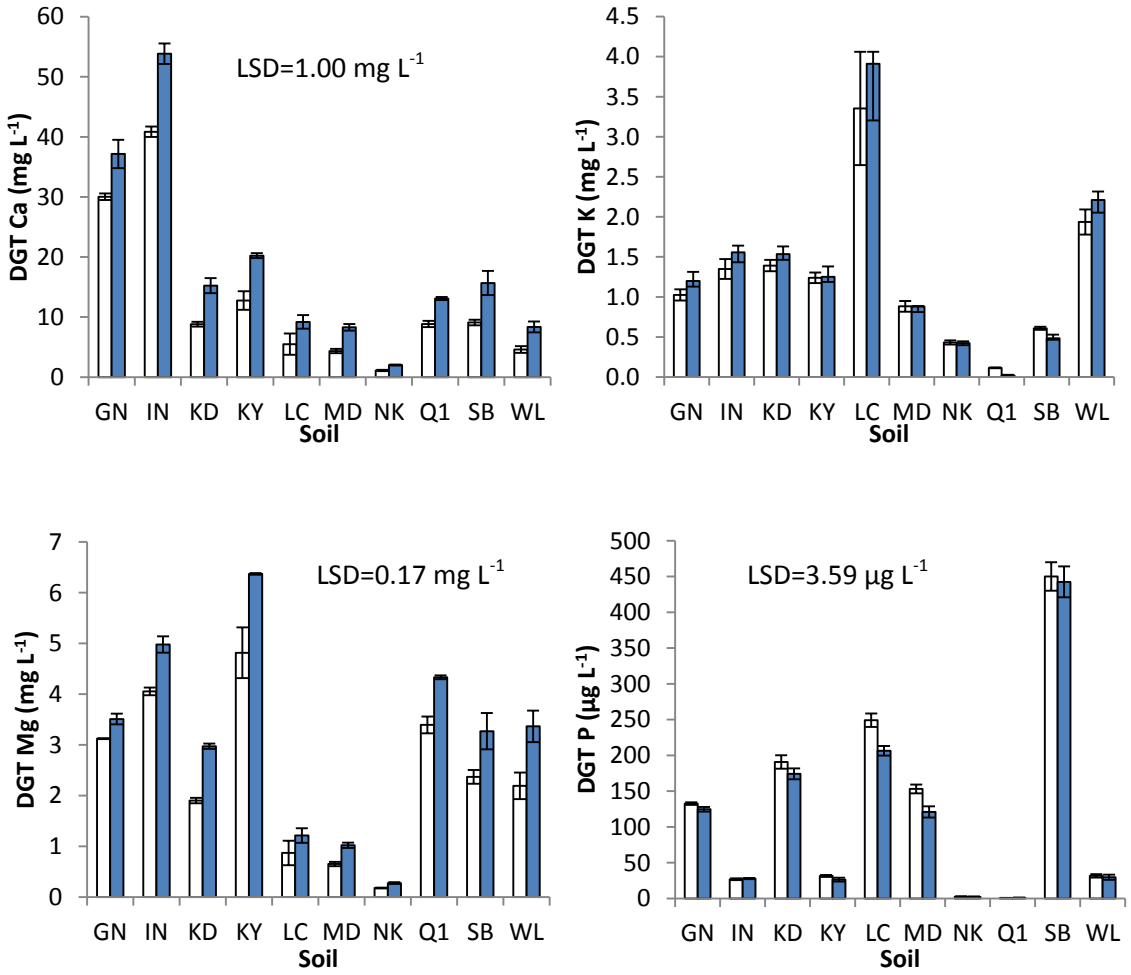


**Fig. A4.1**. Measured DGT values in 10 soils using the MAF gel for a 24 h deployment with fresh diffusive gel (□) and used diffusive gel (■). The presented LSD values mean significant difference was found between two gels at P≤0.05.

4.2. Diffusive gel check

Rinsing the diffusive gel with Milli-Q water significantly reduced the amount of Ca, K, Mg and P on the diffusive gels (Table A4.1). Rinsing the MAF gel with Milli-Q water did not make any difference in the mass of measured element on the diffusive gel. To reuse a diffusive gel, rinsing is likely to be a good means of removing extra elements on the diffusive gel after a DGT measurement. The mass of elements on the diffusive gel is much less than the MDL of the element on resin gel for a DGT test. When the diffusive gel is washed using fresh water flow, rising with a certain velocity, the contamination will possibly be reduced.

**Table A4.1** Measured mass on diffusive gel and the MAF gel with and without Milli-Q water rinsing. U represents gels that are unwashed and W represents washed gels.

| Treatment | | Diffusive gel Mass (μg) | SD of Mass | MAF gel Mass (μg) | SD of Mass |
|---|---|---|---|---|---|
| Ca | | | | | |
| U | 2 | 1.23 | 0.21 | 25 | 2 |
| | 4 | 1.13 | 0.12 | 46 | 3 |
| | 8 | 1.90 | 0.49 | 89 | 7 |
| | 16 | 1.60 | 0.24 | 206 | 16 |
| W | 2 | 0.59 | 0.03 | 23 | 2 |
| | 4 | 0.73 | 0.21 | 45 | 3 |
| | 8 | 0.95 | 0.26 | 95 | 6 |
| | 16 | 0.65 | 0.13 | 200 | 8 |
| K | | | | | |
| U | 2 | 0.22 | 0.11 | 37 | 1 |
| | 4 | 0.23 | 0.16 | 68 | 5 |
| | 8 | 0.89 | 0.24 | 125 | 6 |
| | 16 | 2.50 | 0.56 | 157 | 32 |
| W | 2 | 0.60 | 0.28 | 38 | 2 |
| | 4 | 0.47 | 0.31 | 73 | 4 |
| | 8 | 0.94 | 0.14 | 126 | 4 |
| | 16 | 2.42 | 0.14 | 174 | 21 |
| Mg | | | | | |
| U | 2 | 1.62 | 0.51 | 21 | 3 |
| | 4 | 0.74 | 0.27 | 38 | 3 |
| | 8 | 2.32 | 0.75 | 73 | 6 |
| | 16 | 2.15 | 0.55 | 162 | 8 |
| W | 2 | 0.62 | 0.05 | 20 | 2 |
| | 4 | 0.73 | 0.50 | 39 | 3 |
| | 8 | 1.39 | 0.28 | 78 | 4 |
| | 16 | 1.19 | 0.35 | 160 | 6 |
| P | | | | | |
| U | 2 | 0.03 | 0.00 | 1 | 0 |
| | 4 | 0.03 | 0.00 | 2 | 0 |

| | | | | | |
|---|---|---|---|---|---|
| | 8 | 0.04 | 0.00 | 3 | 0 |
| | 16 | 0.03 | 0.00 | 7 | 1 |
| W | 2 | 0.01 | 0.01 | 1 | 0 |
| | 4 | 0.02 | 0.00 | 2 | 0 |
| | 8 | 0.02 | 0.01 | 3 | 0 |
| | 16 | 0.02 | 0.00 | 8 | 0 |

**References**

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Zhang H, Davison W (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 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.

## Appendix 5: Pictures depicting the main experimental processes

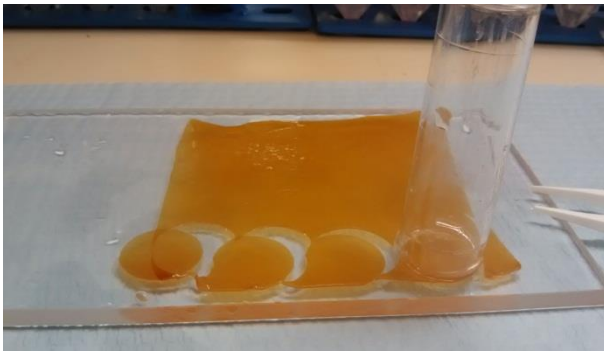

**Fig. A5.1** Cutting the MAF gels

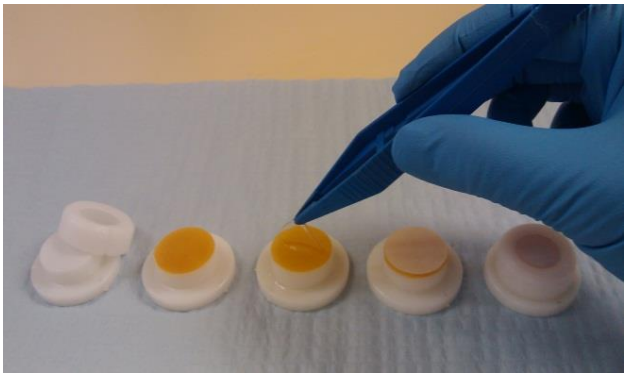

**Fig. A5.2** Preparation of the DGT device

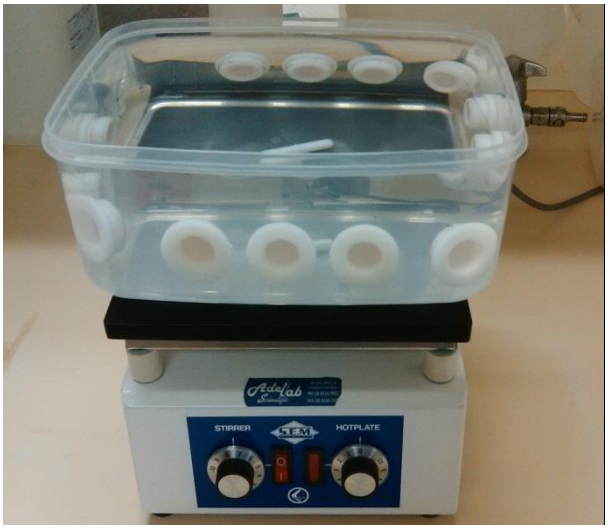


**Fig. A5.3** DGT deployment in a solution test

**Fig. A5.4** DGT deployment in a soil test

**Fig. A5.5** Dismantling the DGT device and elution of the MAF gel

**Fig. A5.6** Wheat grown in the glasshouse