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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 $1.30\times10^{-5}\,\mathrm{cm^2\,s^{-1}}$ at $22\pm1\,^{\circ}\mathrm{C}$ 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

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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:

$$f_e = \frac{c_{\mathrm{Acid}} \times 10.265}{M_{\mathrm{Initial}} - M_{\mathrm{Final}}} \times 100 \tag{1}$$

$$f_u = \frac{M_{\mathrm{Initial}} - M_{\mathrm{Final}}}{M_{\mathrm{Initial}}} \times 100 \tag{2}$$

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:

$$M = M_{\mathrm{Acid}}/f_e \tag{3}$$

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]:

$$D = \frac{slope \times \Delta g}{A \times C_{\mathrm{solution}} \times 60} \tag{4}$$

where "slope" is the measured K amount on gel with deployment time (ng min^{-1}); Δg 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 λ 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.

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.

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] $\mu g\ L^{-1}$	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 ($P \leq 0.05$, $n=3$).

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

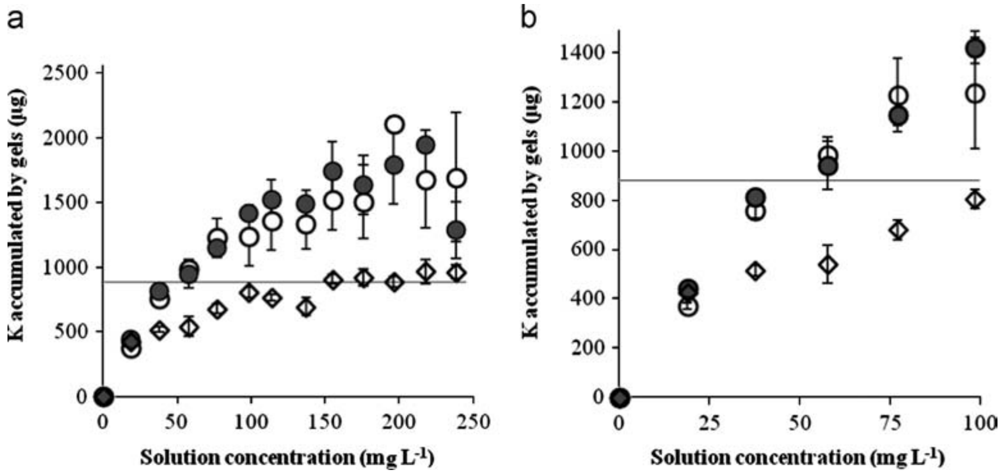

Fig. 1. Accumulation of K by 3 different gels (○ Gel A, ● Gel GA, ◇ Gel GAF) after 24 h in solution differing in K concentration. ((a) all solutions and, (b) solutions with low K concentrations; the horizontal solid line indicates the capacity of 880 μg reported by Tandy et al. [1]). Error bars represent 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 1.30×10^{-5} cm^2 s^{-1} at 22 ± 1 °C was obtained and was only 72% of the value in water (1.81×10^{-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 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.

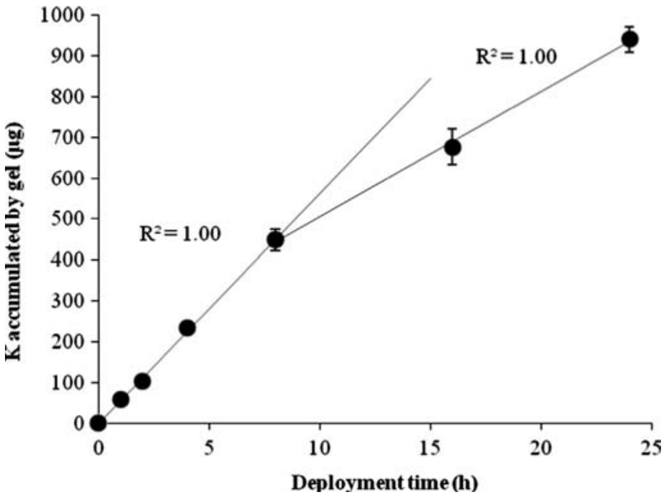

Fig. 2. Accumulation of K by the MAF gel during different deployment periods in 40 mg L^{-1} K solution. Error bars represent standard errors from three replicates.

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 ($P \leq 0.05$, $n=3$).

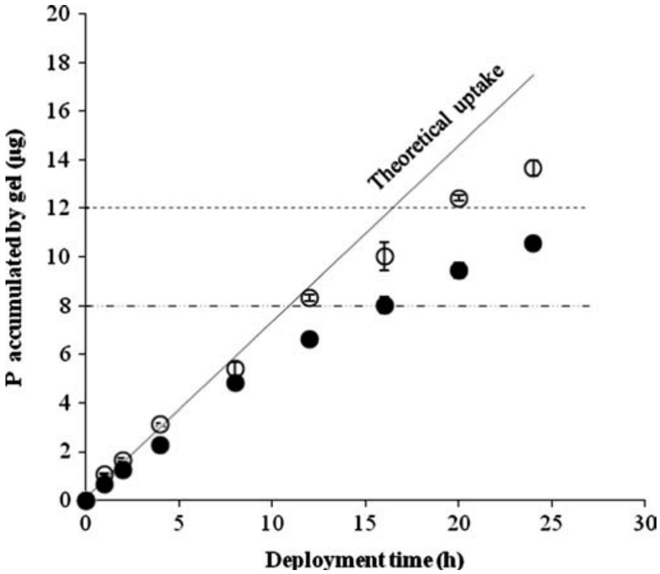

Fig. 3. Accumulation of P from solution (1.2 mg L^{-1} P) by both the MAF gel (●) and ferrihydrite gel (○) at different deployment periods (– – – – indicates the capacity of ferrihydrite gel reported by Mason et al. [33] and —·· — indicates the theoretical capacity of the MAF gel calculated according 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 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.

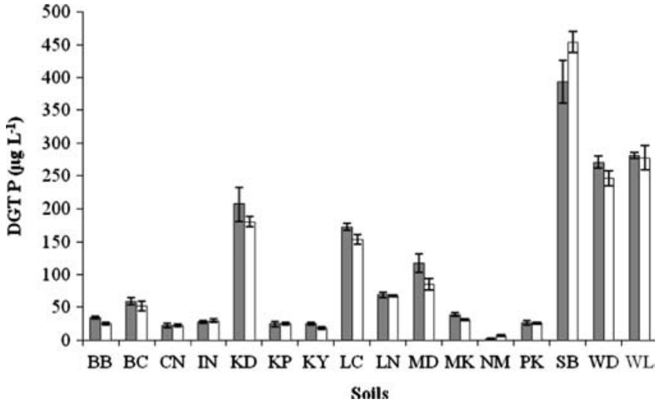

Fig. 4. Concentrations of P accumulated by DGT (expressed as C_{DGT}) in a variety of soils obtained using the MAF gel (▩) and ferrihydrite gel (☐), LSD=7.42 µg L^{-1} at level $P \leq 0.05$. Error bars represent standard errors from three replicates.

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 1.30×10^{-5} cm^2 s^{-1} was obtained for K at 22 ± 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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