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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

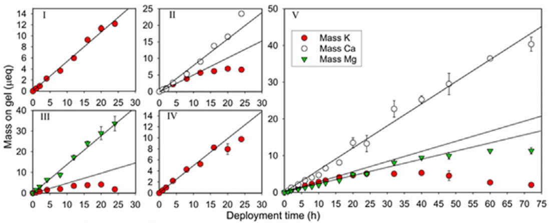
Yulin Zhang [a,*], Sean Mason [a], Ann McNeill [a], Michael J. McLaughlin [a,b]

[a] School of Agriculture, Food and Wine, University of Adelaide, SA 5064, Australia
[b] CSIRO Sustainable Agriculture Flagship, CSIRO Land and Water, PMB 2, Glen Osmond, SA 5064, Australia

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 1.12×10^{-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.

[*] Corresponding author at: 122 Davies Building, University of Adelaide, Waite Campus, Glen Osmond, SA 5064, Australia. Tel.: +61 8 83138114; fax: +61 8 83137109.
E-mail addresses: yulinzhangbest@126.com, yulin.zhang@adelaide.edu.au (Y. Zhang).

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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.