






Evaluation of the diffusive gradients in thin-films (DGT) technique for measuring nitrate and ammonium in soil

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Environmental context. Nitrate (NO_3^-) and ammonium (NH_4^+) are the most important soil nitrogen forms for plant growth. However, conventional extraction techniques may introduce artefacts affecting the measurement of plant-available N concentrations following sampling and sample preparation processes. This is the first study of the DGT technique being used to measure $\text{NO}_3\text{-N}$ and $\text{NH}_4\text{-N}$ in a wide range of soils, compared with conventional KCl extraction, and examined different factors that contribute to the plant-availability of these ions in soils. The knowledge would help to optimise soil nitrogen management practices, increase economic benefits and reduce environmental impacts.

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ABSTRACT

Rationale. The availability of soil nitrogen for plant uptake can be affected by numerous soil factors such as soil texture, moisture and organic matter content, temperature and microbial activity. Conventional extraction techniques may affect the measurement of plant-available N concentrations following sampling and sample preparation processes, including drying, sieving, homogenising, freezing and thawing. The diffusive gradients in thin-films (DGT) technique can overcome some limitations of the conventional extraction techniques and has been used to successfully estimate the plant-available fractions of nutrients, such as P, K, Zn, Cu and Mn in soils. Therefore, it is important to evaluate the use of DGT for measuring NO_3^- and NH_4^+ in a wide variety of soils and examine the factors that contribute to the plant-availability of these ions in soils. **Methodology.** The experiment evaluated the ability of the DGT technique to measure $\text{NO}_3\text{-N}$ and $\text{NH}_4\text{-N}$ in soils using binding layers containing A520E anion exchange resin or Microlite[®] PrCH cation exchange resin, respectively. The DGT results were compared to those from conventional KCl extraction. **Results.** The A520E- and PrCH-DGTs showed good detection limits for $\text{NO}_3\text{-N}$ ($6.90 \mu\text{g L}^{-1}$) and $\text{NH}_4\text{-N}$ ($6.23 \mu\text{g L}^{-1}$) and were able to measure potentially available $\text{NO}_3\text{-N}$ and $\text{NH}_4\text{-N}$ in unfertilised soils. The mass of $\text{NO}_3\text{-N}$ and $\text{NH}_4\text{-N}$ that accumulated on the DGT device increased linearly across soil concentrations ranging from 5 to 300 mg kg^{-1} $\text{NO}_3\text{-N}$ (depending on soil type) and $5\text{--}300 \text{ mg kg}^{-1}$ $\text{NH}_4\text{-N}$; which is equivalent to fertiliser rates of $75\text{--}450 \text{ kg ha}^{-1}$ N. DGTs were used to measure potentially available $\text{NO}_3\text{-N}$ and $\text{NH}_4\text{-N}$ in ten soils with various physical and chemical properties. The DGT results were compared with conventional KCl extraction used to determine soil mineral N. DGT and KCl extraction measured values were significantly correlated with each other for $\text{NO}_3\text{-N}$ ($R^2 = 0.53$; $P\text{-value} < 0.001$), but the relationship between the two measurements was weaker for $\text{NH}_4\text{-N}$ ($R^2 = 0.20$, $P\text{-value} = 0.045$). **Discussion.** The results suggest that the two methods sample different N pools in the soils, with DGT targeting the $\text{NO}_3\text{-N}$ and $\text{NH}_4\text{-N}$ that are available in soil pore water and attached to labile solid phases.

Keywords: accumulation, binding capacity, conventional extraction, correlation, DGT technique, fertiliser efficiency, limit of detection, soil nitrogen availability.

Introduction

Nitrogen (N) is critical for plant growth and, of all the plant macronutrients, has the most complex biogeochemical cycle in soils (Montemurro and Diacono 2016). Among the variety of nitrogen species in soil, nitrate (NO_3^-) and ammonium (NH_4^+) are the most

important nitrogen forms for plant growth (Sharma and Bali 2018) and ecosystem production (Canfield *et al.* 2010). Between 50 and 70% of soil nitrogen is prone to loss (Belete *et al.* 2018) mainly by volatilisation, denitrification, runoff and leaching (Montemurro and Diacono 2016). Increasing global populations require a significant increase in food production (Godfray *et al.* 2010), which in turn requires maintaining plant-available N stocks in agricultural lands (Gruber and Galloway 2008). These can be sustained through fertiliser inputs but minimising losses must also play a key role. Multiple studies have shown that the application of synthetic N fertilisers has increased continuously since the 1960s (Yuan and Peng 2017), with around a 1.5% annual increase from 2015 to 2020 (FAO 2017) forecasted in 2017. Simultaneously, N fertiliser prices have also increased over previous decades; for instance, the global average urea price was USD 187 per metric tonne in 1990 compared to USD 602 in 2013 (Adjesiwor and Islam 2016). However, the over-application of fertiliser is not economically viable (Goulding *et al.* 2008) and leads to negative environmental consequences (Gruber and Galloway 2008). Since the 1960s, nitrogen concentrations in surface waters have increased significantly due to the widespread use of fertiliser, leading to eutrophication (Moss 2008). Additionally, soil acidification (Guo *et al.* 2010), nitrous oxide (N_2O) emission (a type of greenhouse gas) (De Laporte *et al.* 2021) and ozone depletion (Gruber and Galloway 2008) are other issues related to over-fertilisation with N. Accurate measurement of plant-available soil nitrogen concentrations across various soil types would help to optimise soil nitrogen management practices, increase economic benefits and reduce environmental impacts (Giles *et al.* 1975; Du *et al.* 2020).

The availability of soil nitrogen for plant uptake can be affected by numerous soil factors such as soil texture (Tremblay *et al.* 2012), moisture and organic matter content (Qian and Schoenau 1994), temperature and microbial activity (Maynard *et al.* 2007; Canali *et al.* 2011). Conventional extraction techniques may introduce artefacts affecting plant-available N concentrations following sampling and sample preparation processes (e.g. drying, sieving, homogenising, freezing and thawing) (Stark and Hart 1997; Cai *et al.* 2016). Furthermore, the methods to perform these measurements encompass a wide range of different sieving procedures, extractant types and concentrations, soil/extractant ratios and extraction times. This diversity provides a wide range of estimates of N availability and confounds comparisons between studies (McTaggart and Smith 1993; Li *et al.* 2012; Carrillo-Gonzalez *et al.* 2013; Inselsbacher 2014; Homyak *et al.* 2015). One common method to sample mineral N (NH_4^+ and NO_3^-) in soils is to extract these analytes with a 2 mol L^{-1} KCl solution, using a dry soil/extractant ratio of 1:5, 1:10 or 1:20 (w/v) (Schroeder *et al.* 1985; Maynard *et al.* 2007; Rayment and Lyons 2011). This extraction has been used historically to estimate plant-available N (Saha *et al.* 2018) despite suggestions that this method

overestimates NH_4^+ availability because it can extract strongly bound ions that may not be available in the soil porewater for plant uptake (Mengel 1982; Maynard *et al.* 2007). The extensive sample processing used to extract the NH_4^+ from the soil has also been suggested to be an important contributing factor to this limitation (Stark and Hart 1997; Cai *et al.* 2016).

Diffusive gradients in thin-films (DGT) technique has been used to successfully estimate the plant-available fractions of nutrients, such as P, K, Zn, Cu and Mn in soils (Zhang *et al.* 1995; Mundus *et al.* 2012; Six *et al.* 2012; Zhang *et al.* 2013, 2014b; Guan *et al.* 2022). The amount of analyte sampled by DGT depends on the analyte concentration in the soil porewater and its resupply rate from solid into porewater (Harper *et al.* 1998; Sochaczewski *et al.* 2007). These factors can also affect the rate of nutrient uptake by plant roots in soils (Marschner and Rengel 2012). Moreover, DGT deployments in soils are often carried out under similar moisture conditions to those experienced in the field, without the addition of a chelant or solute to promote the release of analytes of interest from the solid phases that may go on to affect soil chemical characteristics (Lehto 2016). It follows that DGT has been found to be effective at predicting plant-available nutrient concentrations, especially when the supply of nutrients to plants is diffusion-limited (e.g. P, Zn and Cu) (Mason *et al.* 2010; Tandy *et al.* 2011; Sun *et al.* 2014; Vogel *et al.* 2020; Guan *et al.* 2022).

The DGT techniques for measuring NO_3^- and NH_4^+ in freshwaters were developed by Huang *et al.* (2016a, 2016b) using A520E and PrCH ion exchange resins, respectively. The authors noted the high capacity of the two resins to bind NO_3^- and NH_4^+ ions, which in turn highlighted the potential of these resins for undertaking DGT measurements of mineral N species in soils. Cai *et al.* (2016) tested the use of SIR-100-HP resin in DGT for measuring NO_3^- in the porewaters of three soils and found good agreement (<10% error) between DGT devices and porewater NO_3^- values from soil solutions that were collected by centrifuging the soils at 5000g for 15 min. Vogel *et al.* (2020) showed that soil NO_3^- and NH_4^+ concentrations measured in one soil using DGT devices equipped with A520E and PrCH resins were comparable with KCl-extracted N under different soil-N application rates and in the presence of nitrification inhibitors. Furthermore, they showed that KCl and DGT extractions performed before and after plant harvesting gave similar patterns of soil NO_3^- and NH_4^+ measurements. However, the experiment only used one soil type and to date, the ability of DGT with A520E and PrCH binding resins to measure soil NO_3^- and NH_4^+ has not been tested across a wide range of soils. Furthermore, a detailed comparison of DGT-available and KCl-extractable N-species and an analysis of the important factors that cause differences between them is lacking. Given the different mechanisms by which the two techniques sample mineral N in soils, a comparison across a range of soil types will increase the understanding of factors

that govern NO_3^- and NH_4^+ solubility. This study aimed to validate the use of DGT for measuring NO_3^- and NH_4^+ in soils with a variety of physical and chemical properties and examine the factors that contribute to the plant-availability of these ions in soils.

Experimental

The DGT technique was evaluated by (1) testing the capability of DGT to measure NO_3^- and NH_4^+ in three unamended soils, (2) measuring the accumulation of these ions in DGTs deployed in the same three soils spiked at 12 N concentrations, and (3) comparing DGT to conventional KCl extraction in ten contrasting soils spiked with two N concentrations.

Soil preparation

Thirteen topsoils (0–10 cm depth) listed in Table 1, were selected from Australian agricultural sites to provide a range of chemical and physical soil properties for evaluating DGT performance. Soils were ground, sieved (< 2 mm) and dried in an oven at 40°C for 2 days until constant weight (Rayment and Lyons 2011). The soil maximum water holding capacity (MWHC) was determined by the gravitational method (Margesin and Schinner 2005). Soil chemical and physical characteristics (pH, electrical conductivity (EC), cation exchange capacity (CEC), texture, total organic carbon (TOC) and total nitrogen) were determined for each soil (Table 1). Extractable mineral nitrogen species (NO_3^- and NH_4^+) were measured in the air-dried soils using a 2 mol L⁻¹ KCl extraction, as described by Rayment and Lyons (2011). Briefly, a 1:5 soil/extractant ratio and 1 h of extraction were employed and the supernatant was analysed after filtering (polyethersulfone, 0.45 μm pore size; Sterlitech Corp., USA). To assist comparison between NO_3^- and NH_4^+ measurements, forthwith their concentrations will be reported as $\text{NO}_3\text{-N}$ and $\text{NH}_4\text{-N}$.

DGT preparation

Reagents

The A520E anion exchange resin and the PrCH cation exchange resin (Purolite Co. Ltd, Asia Pacific, Zhejiang, China) were used as the binding agents in the DGT binding layers. Ultrapure agarose (Life Technologies Corp., USA) was used to prepare the diffusive layer and PrCH binding layer (see below) and bisacrylamide (acrylamide/bis-acrylamide – 40%, Sigma-Aldrich, USA) was used for the A520E binding layer. All reagents were of analytical grade and were purchased from Sigma-Aldrich, Merck and Chem-Supply. All samples and standard solutions were prepared in ultrapure water (Milli-Q[®] Advantage A10, Merck; 18.2 MΩ resistivity). All plastic containers used for the experiments, DGT devices

and glass plates were cleaned in 10% (v/v) HCl (AR-grade, Merck) for a minimum of 24 h, and rinsed thoroughly with ultrapure water prior to use.

Pre-treatment of A520E resin

Preliminary work identified high concentrations of $\text{NO}_3\text{-N}$ in the A520E resin, and this needed to be removed to minimise the possibility of it interfering with the DGT analyses. To optimise the washing procedure, three concentrations of NaCl (1, 2 and 3 mol L⁻¹) were tested over three wash times (24, 48 and 72 h) at two temperatures (20 and 60°C). First, the A520E resin beads were finely ground using an electric grinder and 2.8 (± 0.05) g was measured in triplicate into 50 mL centrifuge tubes and 50 mL of NaCl was added. Tubes were then shaken (end-over-end for 20°C samples, manually every 2–4 h for 60°C samples) for the designated time, and centrifuged for 20 min at 8116g, after which the supernatant was removed. The NaCl solution was refreshed after each 24 h period for the two longer wash times. After washing, the resin was rinsed with ultrapure water to remove any excess NaCl by shaking manually for 2 min and the supernatant was removed after centrifugation (8116g for 20 min). This was repeated until the EC of the supernatant was less than 100 μS cm⁻¹. The washed A520E resin in the centrifuge tubes was frozen (–18°C), freeze-dried for 24 h and then homogenised by manually shaking in a clean polyethylene container prior to use in the binding gels (see below).

Gel layer and membrane preparation

Agarose diffusive gels (0.075 cm thick) were prepared as described previously (Davison and Zhang 1994; Huang *et al.* 2016b). PrCH binding layers were prepared as described by Huang *et al.* (2016b) to a final thickness of 0.075 cm. The A520E binding layer was prepared using the washed A520E resin (washed with 3 mol L⁻¹ NaCl for 72 h, at 20°C), as described by Huang *et al.* (2016a) and cast to a thickness of 0.050 cm. Agarose diffusive gels were stored in 0.001 mol L⁻¹ NaCl, while the A520E and PrCH binding layers were stored in ultrapure water at 4°C before the DGT devices were assembled. Polyethersulfone filter membranes were soaked in ultrapure water for 24 h before use (0.45 μm pore size; Sterlitech Corp., USA).

DGT device preparation

Properly washed DGT devices with an exposure area of 2.54 cm² (DGT Research Ltd., Lancaster, UK) were assembled by layering (1) a binding layer (either A520E or PrCH) at the base, (2) an agarose diffusive layer in the middle and (3) a polyethersulfone filter membrane at the top. The cap of the DGT device was used to seal the assembly and ensure that any solute flux into the resin was through the filter only. For the PrCH-DGT, a 0.025 cm thick spacer ring was used between the base of the device housing and the cap to accommodate the thicker binding layer.

Table 1. Physical and chemical properties of Australian soils^A used in this study.

Evaluation experiment	Soils	Abbreviation	Texture	pH (1:5 water)	EC ^B 1:5 (soil:water, w/v) (mS cm ⁻¹)	TOC (%)	NO ₃ -N KCl (mg kg ⁻¹) ^C	NH ₄ -N KCl (mg kg ⁻¹) ^C	Total N (%)	CEC ^D (cmol kg ⁻¹)	MWHC (g 100 g ⁻¹ soil)
• DGT deployment in unamended soils	Monarto	MO	Silt	7.67	0.15	1.6	3.38	3.47	0.21	23	32.8
	Mallala	MA	Sandy loam	7.79	0.14	1.95	13.25	2.86	0.25	36	42.8
	Ngarkat	NG	Sand	7.14	0.04	0.55	3.18	2.52	0.11	2.9	19.8
• Accumulation test using N spiked soils	Riverland	RL	Sand	8.08	0.34	0.68	2.58	1.47	0.12	11.96	28.0
	Loxton	LX	Sand	9.39	0.21	0.07	1.5	1.0	0.038	16.65	15.7
	Belfrayden	BF	Sandy loam	5.36	0.09	0.74	2.1	7.2	0.19	2.37	18.9
	Badgingarra	BD	Sand	6.35	0.44	0.66	1.8	3.6	0.059	1.78	21.2
	Kalani	KL	Sand	4.33	0.05	0.23	5.0	1.0	0.039	1.44	15.3
	Codering	CD	Gravel	5.73	0.08	3.1	24	4.7	0.17	4.81	27.5
	Wongan Hills	WH	Sand	5.6	0.01	0.45	2.9	1.0	0.16	1.32	17.5
	Brinkworth	BW	Loam	7.52	0.31	1.94	27	2.9	0.41	22.4	34.3
	Port Broughton	PB	Loam	8.1	0.35	1.78	20	2.6	0.23	32.4	37.2
Paris Creek	PC	Clay	6.45	0.18	5.6	29	3.0	0.2	18	51.7	

^AThe locations of the Australian soils are shown in the map in the Supplementary material.

^BEC: electrical conductivity.

^CSoil NH₄-N and NO₃-N values were measured in air-dried soil samples (Rayment and Lyons 2011).

^DExchangeable bases and CEC – 1 mol L⁻¹ ammonium acetate at pH 7.0, rapid method with no pre-treatment for soluble salts (Rayment and Lyons 2011).

Assembled devices were stored in double-sealed plastic bags with 1–2 mL of ultrapure water at 4°C until deployment. Forthwith, the DGT devices used to measure NH₄-N and NO₃-N will be referred to as PrCH-DGT and A520E-DGT, respectively. DGT blank concentrations were measured (see below) from randomly sampled, undeployed devices of both types. The limit of detection (LoD) for both devices was calculated as three times the standard deviation of these blanks (Luo *et al.* 2010).

DGT deployment, elution and analysis

Between 50 and 60 g of each soil was weighed into a Petri dish to a soil bulk density of 1.5 g cm⁻³. The water content was raised to 80% MWHC using ultrapure water and left to equilibrate for 48 h. The DGT devices were then deployed, at 24°C, onto the soil surface, ensuring complete contact with the DGT device window. The deployment time was 20 h (±5 min), unless stated otherwise. At the end of the deployment, the devices were removed and washed thoroughly with ultrapure water, after which the devices were stored in sealed plastic bags with 1–2 mL of ultrapure water at 4°C until disassembly.

The DGT devices were opened using a clean screwdriver and the binding layers were removed with clean plastic forceps. Both types of binding layers were eluted in 2 mL of 2 mol L⁻¹ NaCl for 24 h. The eluents were diluted at least 10 times with ultrapure water and the concentrations of NH₄-N and NO₃-N were measured using a segmented flow analyser, with a high-resolution digital photometer using a colorimetric method (Seal AA3, Seal Analytical, USA). Instrument detection limits were 2.31 µg L⁻¹ for NH₄-N and 1.96 µg L⁻¹ for NO₃-N (*n* = 10). The eluent concentrations were used to determine the total masses of NH₄-N and NO₃-N bound to the resin gel, assuming that 87.2% of the NH₄⁺ and 82.7% of the NO₃⁻ bound to the two types of binding layers were eluted (Huang *et al.* 2016a, 2016b). The DGT-measured concentrations of NH₄-N and NO₃-N in the soil porewater were calculated from the accumulated analyte mass using Eqns 1, 2, respectively (Davison and Zhang 1994); forthwith, these will be expressed as C_{NH₄-N} and C_{NO₃-N}.

$$C_{\text{NH}_4\text{-N}} = \frac{M_{\text{NH}_4\text{-N}} \delta^{\text{MDL}}}{D_{\text{NH}_4} A t} \quad (1)$$

$$C_{\text{NO}_3\text{-N}} = \frac{M_{\text{NO}_3\text{-N}} \delta^{\text{MDL}}}{D_{\text{NO}_3} A t} \quad (2)$$

Here, $M_{\text{NH}_4\text{-N}}$ and $M_{\text{NO}_3\text{-N}}$ are the masses of NH₄-N or NO₃-N (ng) bound to the PrCH and A520E binding layers, respectively, δ^{MDL} is the total thickness of the material diffusion layer (i.e. filter and diffusion layer: 0.089 cm), D_{NH_4} and D_{NO_3} are the diffusion coefficients of NH₄⁺ (Huang *et al.* 2016b) and NO₃⁻ (Huang *et al.* 2016a) through the material diffusion layer (cm² s⁻¹, corrected for temperature and EC), t is the deployment time (s) and A is the exposure area of the device to the soil (2.54 cm²).

DGT validation for ammonium and nitrate measurement in soils

DGT deployment in unamended soils

The ability of PrCH- and A520E-DGT to measure low concentrations of NH₄-N and NO₃-N was assessed by deploying them in three contrasting unamended topsoils (Monarto, Mallala and Ngarkat) (Table 1). They were selected based on different soil textures, EC, CEC, inorganic nitrogen and organic matter concentrations. Soils were incubated as described above in *DGT deployment, elution and analysis*, after which subsamples were collected for DGT deployment and KCl extraction. The DGT devices were deployed in triplicate for 24 h to measure C_{NH₄-N} and C_{NO₃-N}, as described earlier. A 2 mol L⁻¹ KCl extraction (see below in *Mineral nitrogen species measurement using 2 mol L⁻¹ KCl extraction of moist soils*) was carried out on a separate moist subsample, 12 h after the start of the DGT deployment.

Accumulation of NH₄-N and NO₃-N in PrCH- and A520E-DGT

The performance of the PrCH- and A520E-DGT to measure NH₄-N and NO₃-N across a wide range of soil-N concentrations was tested using the same three soils as for the DGT deployment in unamended soils (see above). Two stock solutions containing either 2000 or 5000 mg L⁻¹ of NO₃-N were prepared using calcium nitrate, and a further two stock solutions with the same NH₄-N concentrations were prepared using ammonium sulfate. The stock solutions were used to prepare a range of N spike solutions that contained NO₃-N and NH₄-N in concentrations of 5, 10, 20, 30, 40, 50, 75, 100, 150, 200, 250 and 300 mg kg⁻¹. The pHs of the spike (NO₃-N and NH₄-N) solutions were adjusted to pH 7 using 0.01 mol L⁻¹ NaOH, after which they were used to increase the N content of 150 g subsamples of the three different soils. The soil moisture levels were then raised to 80% of MWHC and the soils were left to equilibrate for 48 h. PrCH- and A520E-DGT were deployed in triplicate in N treated soils for 20 h in an incubator (at 24 °C) to measure C_{NH₄-N} and C_{NO₃-N}, as described previously. These deployments were shorter than the typical 24 h to minimise the loss of mineral N from soils through microbial assimilation, denitrification or volatilisation and reduce the possibility of saturating the binding layers. Subsamples of each treatment underwent 2 mol L⁻¹ KCl extraction (see below for details) and pH and EC measurements, in triplicate, 10 h after the start of the DGT deployment.

DGT deployment in a wide range of soils

To further explore the effect of soil characteristics on DGT and 2 mol L⁻¹ KCl-extracted N concentrations, and the differences between them, an experiment was undertaken in ten contrasting soils (Table 1) varying in texture, pH (4.33–9.39), EC (0.01–0.44 mS cm⁻¹), organic matter content (0.07–3.1%) and CEC (1.32–32.4 cmol kg⁻¹).

The soils were incubated at 24°C for 2 weeks at 60% of MWHC, after which the N stock solutions (described above) were used to increase NH₄-N and NO₃-N concentrations to either 50 or 100 mg kg⁻¹ of NH₄-N and NO₃-N (i.e. 100 and 200 mg kg⁻¹ increase in total N, respectively). The soil moisture level was then raised to 80% of MWHC and samples were incubated for another 24 h. C_{NH₄-N} and C_{NO₃-N} were measured in triplicate following 20 h DGT deployment at 24 °C, as described previously. Subsamples of each treatment underwent 2 mol L⁻¹ KCl extraction (see next) and pH and EC measurements in triplicate at the beginning and end of the DGT deployments (Supplementary Fig. S3).

Mineral nitrogen species measurement using 2 mol L⁻¹ KCl-extraction of moist soils

Moist soil (80% of MWHC) samples were extracted with 2 mol L⁻¹ KCl using a 1:5 (dry soil/KCl, w/v) ratio. The volume of the extractant was adjusted (<8%) to compensate for the soil moisture content and to ensure the soil/solution ratio was 1:5 on a dry soil basis. The samples were shaken on an end-over-end shaker for 1 h, after which the supernatant was settled for 1 h and filtered (0.45 µm pore size) (Rayment and Lyons 2011). The filtered extracts were diluted (10–100 times) with ultrapure water prior to analysis with the Seal AA3 segmented flow analyser, as described above. The soil concentrations of NH₄-N and NO₃-N extracted using 2 mol L⁻¹ KCl are reported forthwith as E_{NH₄-N} and E_{NO₃-N}, respectively.

Statistical analysis

The Kolmogorov–Smirnov test was used to confirm that the data were normally distributed and homogeneity of variance between factors was confirmed using Levene's test. The different resin purification methods were compared by the *T*-test based on resin NO₃-N per device. Regression analysis was used to identify the linear response of DGT to soil nitrogen concentrations and compare two soil-N measuring methods (DGT and KCl). The coefficient of determination (*R*²) was used to determine the strength of relationships. Multiple regression analysis was used to examine the effect of various soil factors on NH₄-N measured using different tests. For all analyses, the significance level was 0.05. Analyses were performed using Excel (Microsoft Office 365) and SPSS (IBM, version: 26).

Results and discussion

Blanks and LoD of DGTs and KCl

Initially, the mass of NO₃-N in the blank DGT device with unwashed A520E resin was 13.0 ± 0.79 µg per device (*n* = 10), corresponding to a LoD of 53.0 µg L⁻¹. These values are substantially higher than those from previous

reports (e.g. blank = 1.68 µg L⁻¹ and LoD of 13.15 µg L⁻¹ Huang *et al.* 2016a, 2017), and may have been caused by contamination during manufacturing, subsequent packaging, transport or any combination of these. Therefore, the resin was washed before it was used in the DGT. Washing with 3 mol L⁻¹ NaCl for 72 h at 60°C resulted in the lowest average mass of NO₃-N per device (1.31 µg, Supplementary Fig. S2). Performing this washing at room temperature resulted in slightly less NO₃-N being removed from the resin and thus, a slightly higher mass of NO₃-N per device (1.73 µg). However, the difference was not significant (*P*-value = 0.56), so the resins were washed at room temperature for all subsequent experiments as it is more practical and economical. The LoD for the A520E-DGT (using washed resin) was 6.90 µg L⁻¹ (limit of quantitation (LoQ) of 23 µg L⁻¹) which is within the range of previous studies (1.11–13.15 µg L⁻¹; Table 2) (Huang *et al.* 2016a, 2017; Ren *et al.* 2020).

The average mass of NH₄-N in the blank PrCH resin binding layers was 1.01 ± 0.03 µg, giving the C_{NH₄-N} a LoD of 6.23 µg L⁻¹ (LoQ 20.7 µg L⁻¹). These values are within the range of values determined in previous studies (Huang *et al.* 2016b, 2017; Ren *et al.* 2020) (Table 2).

For KCl extraction, the LoD (1.97 and 2.22 mg kg⁻¹ for E_{NH₄-N} and E_{NO₃-N}, respectively) and LoQ (6.57 and 7.42 mg kg⁻¹ for E_{NH₄-N} and E_{NO₃-N}, respectively) were calculated as three times (LoD) and ten times (LoQ) the standard deviation of three blank 2 mol L⁻¹ KCl extracts.

Measuring low concentrations of N in unamended agricultural soils

Measurements with PrCH- and A520E-DGT confirmed that these binding layers can be used to measure low concentrations of NH₄⁺ and NO₃⁻ in soils. The lowest NH₄-N concentration identified using PrCH-DGT and the 2 mol L⁻¹ KCl extraction tests was in the Ngarkat soil (112 µg L⁻¹ and 8.05 mg kg⁻¹ for C_{NH₄-N} and E_{NH₄-N}, respectively) (Table 3). The mean C_{NH₄-N} and E_{NH₄-N} concentrations in this soil were 5.4 and 1.2 times higher than their respective LoQs. The two tests disagreed on the soil with the highest available NH₄-N concentration: the highest C_{NH₄-N} was measured in the Monarto soil (257 µg L⁻¹), while the Mallala soil had the highest E_{NH₄} (47.1 mg kg⁻¹) (Table 3). This indicates that the two tests measure different pools of NH₄-N in the soils. This is further discussed below when comparing DGT to conventional KCl extraction. The NO₃-N concentrations measured in the three soils by the A520E-DGT and 2 mol L⁻¹ KCl extraction followed the same trend: the highest concentrations were found in the Monarto soil (C_{NO₃-N} 552 µg L⁻¹; E_{NO₃-N} 23.1 mg kg⁻¹), while the lowest concentrations were measured in the Mallala soil (C_{NO₃-N} 11.1 µg L⁻¹; E_{NO₃-N} was below the LoD) (Table 3). In the Mallala soil, the mean C_{NO₃-N} was 50% of the LoQ.

Because DGT accumulates analyte over its full deployment time, the LoD and LoQ can be improved for many

Table 2. Summary of the limit of detection (LoD) values for different binding layers for NO₃-N and NH₄-N.

Nitrogen	Binding layer	Experiment details	LoD values (C _{DGT} µg L ⁻¹)	Mass of analyte in blank DGT (µg per device)	Reference
NO ₃ -N	A520E	<i>In situ</i> deployment in freshwater	1.68–13.15	–	Huang <i>et al.</i> (2016a, 2017)
	AMI	<i>In situ</i> deployment in freshwater	2.02	–	Huang <i>et al.</i> (2016c)
	SIR-100-HP	Soil experiment	3.9 (4h) and 0.7 (24h)	–	Cai <i>et al.</i> (2016)
	ZrO-AT	<i>In situ</i> deployment in natural freshwater	1.11	0.09	Ren <i>et al.</i> (2020)
	A520E	Before NaCl wash	53.0	13.0	The present study
	A520E	After 3 mol L ⁻¹ NaCl 72 h wash at room temperature, used for soil experiment	6.90	1.73	The present study
NH ₄ -N	PrCH	<i>In situ</i> deployment in freshwater	0.42–6.73	–	Huang <i>et al.</i> (2016b, 2017)
	CMI	<i>In situ</i> deployment in freshwater	0.31	–	Huang <i>et al.</i> (2016c)
	Biochar-Zeolite-ZrO	<i>In situ</i> deployment in freshwater	10.0	2.42	Feng <i>et al.</i> (2018)
	ZrO-AT	<i>In situ</i> deployment in natural freshwater	1.01	0.09	Ren <i>et al.</i> (2020)
	PrCH	Soil experiment	6.23	1.01	The present study

Table 3. Soil NH₄-N and NO₃-N concentrations were measured using DGT (C_{NH₄-N} and C_{NO₃-N}) and 2 mol L⁻¹ KCl extraction (E_{NH₄-N} and E_{NO₃-N}) in unamended soils.

Soil ^A	Measured NH ₄ -N		Measured NO ₃ -N	
	C _{NH₄-N} (µg L ⁻¹)	E _{NH₄-N} (mg kg ⁻¹)	C _{NO₃-N} (µg L ⁻¹)	E _{NO₃-N} (mg kg ⁻¹)
Monarto	257 ± 28.1	20.5 ± 0.83	552 ± 286	23.1 ± 5.32
Mallala	234 ± 27.3	47.1 ± 2.75	11.1* ± 1.73	1.05** ± 0.40
Ngarkat	112 ± 90.1	8.05 ± 2.45	37.8 ± 5.60	4.82* ± 0.13

^AResults show mean values ± standard deviation (n = 3). * and ** indicate that mean values are lower than the LoQ and LoD, respectively.

analytes by using longer deployments to allow for greater accumulation on the binding layer (Österlund *et al.* 2016). This ostensibly also applies to NH₄⁺ and NO₃⁻; however, the extent to which long deployment times can be employed to provide accurate concentrations of these analytes in soils at a specific point in time can be limited by the variety of natural processes that can change their concentrations during the deployment. For example, Li *et al.* (2020) reported a mean global nitrification rate of 3.82 mg kg⁻¹ day⁻¹, with higher rates in warm, moist and basic soils with high microbial biomass and abundant nitrogen. It follows that, when nitrification is the dominant process and occurring at a fast rate, measurements of C_{NH₄-N} and C_{NO₃-N} are likely to result in progressively lower and higher values, respectively, for the two analytes when increasing deployment times. However, this does provide the opportunity to use different-length DGT deployments to provide unique information on the dynamics of these N species, where possible artefacts caused by extensive soil manipulation are minimised.

Operational NH₄-N and NO₃-N soil concentration range for PrCH- and A520E-DGT

Accumulation of NH₄-N on the PrCH-DGT increased linearly in all three soils when the soil concentration increased to 300 mg kg⁻¹ (P-value = 0.001; Fig. 1a, c, e). However, the rate of NH₄-N mass accumulation to the device varied between the soils in the order Mallala < Monarto < Ngarkat (0.67, 0.95 and 2.98 µg NH₄-N accumulated per mg kg⁻¹ increase in soil NH₄-N concentration, respectively; Fig. 1). These differences in accumulation rate are most likely due to differences in the soils' capacity to supply NH₄⁺ to the DGT (see next section). At the highest NH₄-N application rate, the DGT device had accumulated between 170 and 900 µg NH₄-N per device in the three soils without evidence to suggest that the mass accumulated in the binding layer of the DGT device was approaching maximum capacity. The maximum amounts of NH₄-N bound onto the PrCH-DGT here are over three times lower than what was observed in fresh waters by Huang *et al.* (2016b) (2990 µg device⁻¹ equivalent to 952 µg cm⁻² Table 4). The 300 mg kg⁻¹ NH₄-N application rate here corresponds to an area application rate of 450 kg N ha⁻¹ (assuming a topsoil depth of 10 cm and a bulk density of 1.5 g cm⁻³), which is at the upper end of N application rates to most agricultural soils (Di and Cameron 2002; GRDC 2017). This suggests that the PrCH-DGT can be used to measure soil NH₄-N concentrations in most agricultural soils.

The accumulation was linear between 0 and 300 mg kg⁻¹ added NO₃-N in the Mallala and Ngarkat soils (P-value < 0.05) (Fig. 1d, f), and in both soils up to 300 µg NO₃-N was bound in the DGT without evidence that the binding capacity of the DGT device had been exceeded. However, the binding capacity was reached in the Monarto soil once

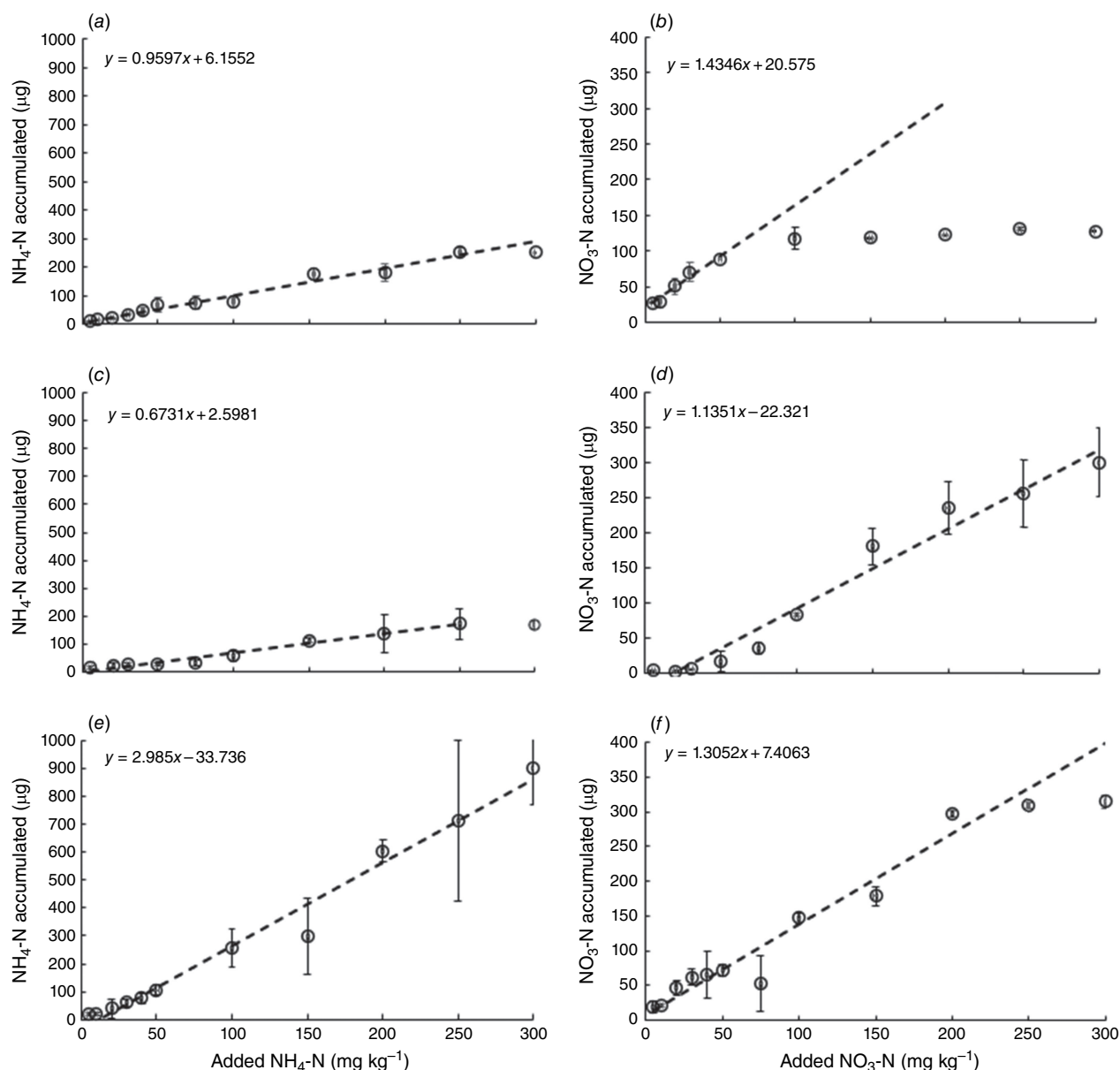


Fig. 1. Mass of NH₄-N accumulated (µg) in PrCH-DGT in (a) Monarto, (c) Mallala and (e) Ngarkat soils. Mass of NO₃-N accumulated (µg) in A520E-DGT in (b) Monarto, (d) Mallala and (f) Ngarkat soils. The dash-lines represent the linear regression models and error bars show standard deviations ($n = 3$).

the mass accumulated NO₃-N exceeded 95 µg (Fig. 1b). The NO₃-N accumulation in the binding layer was linear only until that point (between 0 and 50 mg kg⁻¹ added NO₃-N; P -value = 0.001). This value is over three times higher than the highest reported NO₃-N accumulation in a soil deployment by Cai *et al.* (2016) using the SIR-100-HP-DGT (Table 4). Within the linear ranges of the three soils, the accumulation rate of NO₃-N on the A520E-DGT was similar in all three soils: 1.43, 1.13 and 1.30 µg NO₃-N accumulated per mg kg⁻¹ increase in soil NO₃-N concentration for Monarto, Mallala and Ngarkat soils, respectively (Fig. 1).

Accumulation of NO₃-N into the A520E-DGT can be limited by competition for the resin binding sites with other anions (Huang *et al.* 2016a). While the A520E-DGT has a greater affinity for NO₃⁻ than other commonly found anions in soils, such as HCO₃⁻, SO₄²⁻ and Cl⁻ (Gu *et al.* 2004; Huang *et al.* 2016a), these ions limit the binding of NO₃⁻ when present together in high concentrations. Soil EC can be used as a proxy for the total dissolved ionic solids' concentration in soil (Friedman 2005). For all NO₃-N concentrations added to the Monarto soil, EC values (0.19–1.0 mS cm⁻¹) were higher than those measured in the Ngarkat (EC: 0.19–0.74 mS cm⁻¹)

and Mallala (EC: 0.05–0.63 mS cm⁻¹) soils. The EC values in the Monarto soil align with the previously identified upper conductivity value of 1 mS cm⁻¹ where the resin's capacity for binding NO₃⁻ is reduced due to ion competition (Huang *et al.* 2016a). A conservative upper limit of A520E-DGT for measuring NO₃-N in soils is therefore 50 mg NO₃-N kg⁻¹ (equivalent to 75 kg ha⁻¹ of NO₃-N, in the 10 cm of topsoil with a bulk density of 1.5 g cm⁻³), which is generally above the range of soil NO₃-N concentrations recommended for agricultural production (Department of Employment Economic Development and Innovation 2010) and among the highest application rates of USA and China (Zhang *et al.* 2015). In most cases, a soil-N test is performed prior to sowing to estimate potential soil-N supply before soil-N application;

Table 4. Maximum soil-N accumulation to PrCH- and A520E-DGTs in three experimented soils (Monarto, Mallala and Ngarkat) and freshwater.

DGTs		Maximum N accumulation reported (µg cm ⁻²)	Water/soil porewater conductivities (mS cm ⁻¹)
PrCH-DGT	Freshwater	952 ± 61.7 ^{A,B}	0.35 ^B
	Monarto	99.7 ± 6.29	0.19–1.0
	Mallala	68.1 ± 21.1	0.19–0.63
	Ngarkat	355 ± 52.4	0.05–0.74
A520E-DGT	Freshwater	270 ± 7.64 ^{A,C}	0.35
	Monarto	37.4 ± 7.26 ^A	0.19–1.0
	Mallala	118 ± 19.2	0.19–0.63
	Ngarkat	117 ± 1.72	0.05–0.74
SIR-100-HP-DGT	Soils	5.74 ^D	

^AEstablished as the binding capacity of the DGT device in that medium. ^BHuang *et al.* (2016b), ^CHuang *et al.* (2016a), ^DCai *et al.* (2016) estimated from soil deployment, assuming 20 h deployment and resin gel area of 4.91 cm².

therefore, the maximum binding capacity is sufficient for soil-N tests. Concentrations exceeding this limit are rare, except under specific circumstances such as animal urine patches (Di *et al.* 2009; Orwin *et al.* 2009). In such cases, EC measurements should be used to confirm that ion competition is unlikely to affect the C_{NO₃-N} measurement.

Because the capacity of the PrCH-DGTs was not exceeded, and the capacity of A520-DGTs was only exceeded in one instance (NO₃-N in Monarto soil), it is unsurprising that the highest amounts of solute bound to the resin layers are lower than the capacities reported in solution measurements by Huang *et al.* (2016a, 2016b) (Table 4). However, the results reported here can inform the upper operational limit for using these binding layers in DGT soil-N measurements. Any results where the mass of N accumulated exceeds these values should be interpreted with caution.

Comparison of DGT to conventional KCl-extraction for measuring NH₄-N and NO₃-N in contrasting soil types

Positive correlations were found between C_{NH₄-N} and E_{NH₄-N} measurements ($R^2 = 0.20$; P -value = 0.045) and between C_{NO₃-N} and E_{NO₃-N} measurements ($R^2 = 0.53$; P -value < 0.001) in the ten soils amended with two rates of N (50 and 100 mg kg⁻¹ of NH₄-N and NO₃-N) (Fig. 2). The stronger correlation between C_{NO₃-N} and E_{NO₃-N} is likely to be due to NO₃⁻ anions generally adsorbing weakly to soil solid phases: mainly as diffuse-ion swarm species or as outer-sphere surface complexes (Sposito 2008). Consequently, differences in the mechanisms by which the ion is sampled by the two techniques may be expected to have a less pronounced effect on the amount measured.

Analysis of E_{NH₄-N} and C_{NH₄-N} among the different soils revealed that soil CEC can play a significant role in the relative amounts of NH₄⁺ sampled by the two techniques. In the soils with low CEC (1.32–4.81 cmol kg⁻¹), the correlation between C_{NH₄-N} and E_{NH₄-N} measurements increased

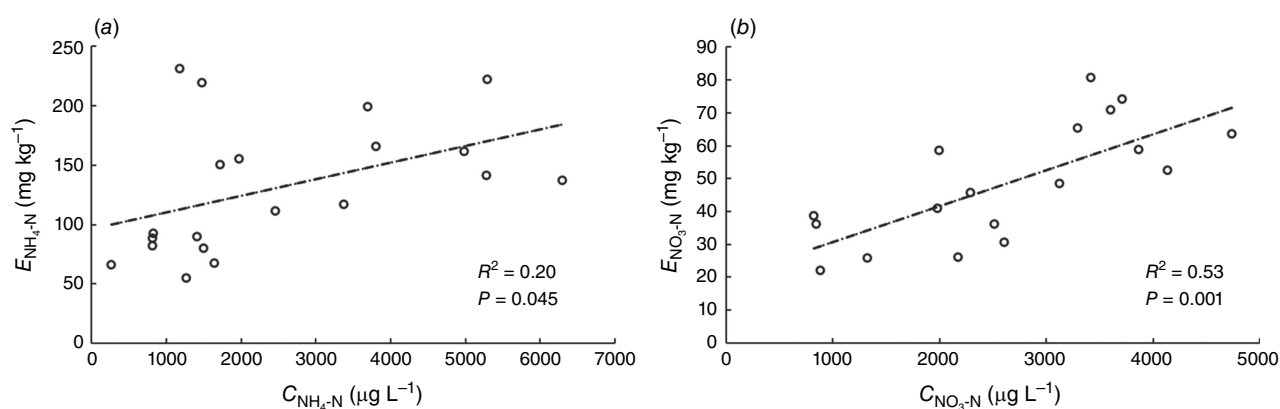


Fig. 2. Comparison of DGT- and KCl-measured soil (a) NH₄-N and (b) NO₃-N in ten different soils amended with either 50 or 100 mg kg⁻¹ of NH₄-N and NO₃-N using three replicates. The dotted lines show the best fit linear regression models.

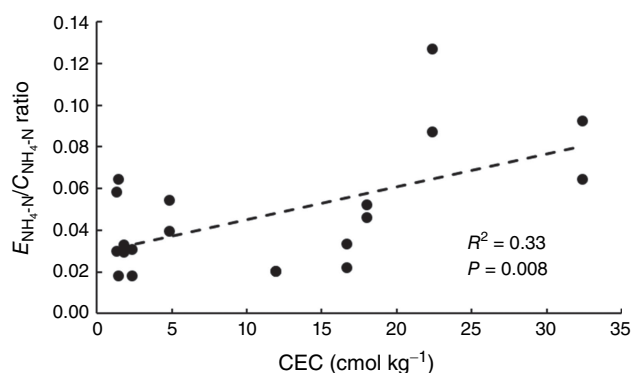


Fig. 3. Relationship between $E_{\text{NH}_4\text{-N}}/C_{\text{NH}_4\text{-N}}$ ratio and soil CEC.

($R^2 = 0.53$, P -value < 0.05 , 10 soil samples: five soils at two concentrations, shown in Supplementary Fig. S4), while the relationship was not significant in the soils where CEC was greater than $11.9 \text{ cmol kg}^{-1}$ ($R^2 = 0.12$, P -value > 0.05 ; 10 soil samples: five soils at two concentrations, shown in Supplementary Fig. S4). A comparison of the amount of $\text{NH}_4\text{-N}$ measured by the two techniques in soils with different CECs found that the soils' ability to supply NH_4^+ to the PrCH-DGT decreases with higher CEC when compared to the amount sampled by the 2 mol L^{-1} KCl extract (Fig. 3). Soil CEC also co-varied negatively with the rate of $\text{NH}_4\text{-N}$ mass accumulation by DGT when different amounts of $\text{NH}_4\text{-N}$ were applied to three soils (see the previous section for details). In that experiment, the CEC of the three soils Mallala (36 cmol kg^{-1}), Monarto (23 cmol kg^{-1}) and Ngarkat (2.9 cmol kg^{-1}) was inversely related to the rate at which $\text{NH}_4\text{-N}$ supply to the DGT increased with $\text{NH}_4\text{-N}$ application to the soil (Table 2, Fig. 1 a, c, e).

The role of CEC may be rationalised by the dynamics of soil chemical processes. The supply of solute to DGT is thought to be determined partly by the resupply from sorbed solute when porewater concentrations are depleted (Zhang et al. 2014a; Lehto 2016; Marrugo-Madrid et al. 2021), but the extent of this resupply can be limited by the rate of desorption during the measurement time (Harper et al. 1998; Lehto et al. 2008). On the other hand, the 2 mol L^{-1} KCl extraction assumes an equilibrium between solid and solution phases and relies on ion-exchange between K^+ and the similar size NH_4^+ ions sorbed to soil colloids (Mulvaney 1996). The difference in the amount of NH_4^+ measured by the two techniques may be partly due to the ion exchange reaction in the extraction overcoming the kinetic limitation to solid phase $\text{NH}_4\text{-N}$ supply to the DGT. A further factor contributing to the difference may be the role of soil pH that had an exponential relationship with CEC ($\text{CEC} = 0.086 \times e^{0.6413\text{pH}}$, P -value < 0.05 , Supplementary Fig. S5). Four of the ten soils tested had $\text{pH} > 7$ and may have lost some NH_4^+ through volatilisation as ammonia gas during measurements. Losses through volatilisation may have been exacerbated by the warm temperature, high soil moisture content, the use of

ammonium sulfate to add $\text{NH}_4\text{-N}$ and that pH has a stronger effect than CEC in affecting volatilisation (Powlson and Dawson 2021). In addition, there would have been more time for NH_4^+ to be lost during the 20 h DGT deployment than the shorter KCl extraction (usually $< 2 \text{ h}$). This suggests that DGT measurements of $\text{NH}_4\text{-N}$ should be ideally carried out quickly, under cooler conditions and in acidic soils to minimise losses of the analyte during the deployment.

Conclusions

This is the first study in which PrCH- and A520E-DGT were evaluated to measure $\text{NH}_4\text{-N}$ and $\text{NO}_3\text{-N}$ in a variety of soils with a wide range of soil-N concentrations and soil properties. The PrCH- and A520E-DGT were able to detect and quantify low concentrations of the two mineral N species in low fertility soils. The two types of DGT, PrCH- and A520E-DGT, can also be used to measure soil $\text{NH}_4\text{-N}$ and $\text{NO}_3\text{-N}$ concentrations at most agriculturally relevant soil concentrations; however, for $\text{NO}_3\text{-N}$ measurements, complementary measurements of EC are recommended to help ensure that resin binding saturation does not affect the results. When compared against the more commonly used 2 mol L^{-1} KCl extraction, DGT appears to sample a different pool of $\text{NH}_4\text{-N}$ in soils and the strengths of the technique may lie in investigations into the sorption dynamics of the solute. However, such measurements should seek to minimise losses of the solute during the measurement through volatilisation to ensure accurate results.

Supplementary material

Supplementary material is available [online](#).

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