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Assessing plant-available glyphosate in contrasting soils by diffusive gradient in thin-films technique (DGT)

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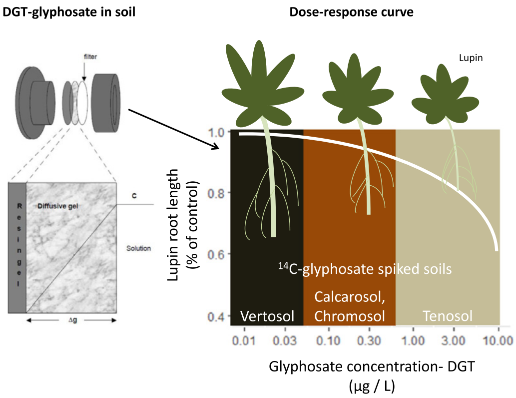
HIGHLIGHTS

- A DGT method was developed to assess the available glyphosate.
- A threshold toxicity of glyphosate to wheat and lupin was quantified across four soils.
- This technique can be used in the risk assessment of herbicide residues in soils.

GRAPHICAL ABSTRACT



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ABSTRACT

Glyphosate represents one quarter of global herbicide sales, with growing interest in both its fate in soils and potential to cause non-target phytotoxicity to plants. However, assessing glyphosate bioavailability to plants from soil residues remains challenging. Here we demonstrate that the diffusive gradient in thin-films technique (DGT) can effectively measure available glyphosate across boundary conditions typical of the soil environment: pH 4–9, P concentrations of 20–300 μg P L^{-1} and $NaHCO_3$ concentrations of 10–1800 mg L^{-1}. In this study, four soils with different glyphosate sorption properties were dosed with up to 16 mg kg^{-1} of glyphosate and phytotoxicity to wheat and lupin was measured against the DGT-glyphosate concentrations. An improved dose response curve was obtained for root elongation of wheat and lupin across soil types when DGT-glyphosate was used instead of alkaline-extractable (i.e., total extractable) glyphosate. Total extractable glyphosate concentrations of 2.6 and 5.0 mg glyphosate kg^{-1} in the sandy Tenosol, equivalent to 2.9 and 6.5 μg L^{-1} DGT-extractable glyphosate, reduced the root length of lupins (but not wheat) by 32–36% compared with the untreated control. DGT is therefore a promising method for assessing phytotoxic levels of glyphosate across different soils.

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1. Introduction

Glyphosate [*N*-(phosphonomethyl) glycine] is a broad spectrum, non-selective systemic, post-emergent herbicide used for weed control in agricultural and urban environments. The commercialisation of glyphosate-tolerant crops in 1996 (Benbrook, 2012) has resulted in increased glyphosate use, and glyphosate now represents one-quarter of global herbicide sales (GSBR, 2011). Because of its widespread application, a growing body of research has focused on assessing the fate and risks of glyphosate residues in soil, water and food (Williams et al., 2000; Borggaard and Gimsing, 2008; Helander et al., 2012; Kanissery et al., 2015).

Glyphosate has a propensity to bind to soil particles, which reduces its mobility, bioavailability and risk to non-target organisms. The dominant binding mechanism involves the phosphonic acid moiety interacting with positively charged sites on clay minerals, notably aluminium and iron (hydr)oxides (Sprankle et al., 1975; Shushkova et al., 2010). Because glyphosate is zwitterionic, interaction of the amine group in glyphosate with negatively charged soil/colloidal particles and functional groups in soil organic matter can also contribute to sorption, albeit to a lesser extent (Borggaard and Gimsing, 2008).The influence of soil organic carbon content on glyphosate sorption is not consistent (Farenhorst et al., 2009), with some studies reporting that soil organic carbon (SOC) content decreased glyphosate sorption (Arroyave et al., 2016; Day et al., 1997), while others suggest that SOC increased glyphosate sorption (Piccolo et al., 1996; Albers et al., 2009). Glyphosate can also bind with negatively charged organic matter through di/trivalent cation bridging (dissolved cations, Ca^{2+}, Al^{3+} and Fe^{2+}, Barrett and McBride, 2007) and also with divalent cations in 2:1 clay minerals (Glass, 1987; Piccolo et al., 1994).

Nevertheless, in certain soils or under particular environmental conditions, glyphosate sorption can be limited, leaving a significant fraction of labile glyphosate that is more amenable for biological uptake or off-site movement (Barja and dos Santos Afonso, 2005; Borggaard and Gimsing, 2008; Al-Rajab and Schiavon, 2010). Light-textured soils with low iron or aluminium (hydr)oxide mineral content generally have a lower capacity for glyphosate sorption (Piccolo et al., 1994) which can increase the risk of crop seedling damage relative to heavier-textured soil types (Bott et al., 2011). These soils are also more susceptible to leaching and runoff losses of glyphosate (Piccolo et al., 1994). The presence of anions which compete for soil sorption sites, particularly inorganic phosphate, is another factor that can lower glyphosate sorption (Dion et al., 2001; Gimsing et al., 2004a) leading to increased bioavailability and potential phytotoxicity (Bott et al., 2011; Cornish, 1992). Soil pH regulates the charge density of both glyphosate and clay minerals, such that neutralisation of soil pH has a tendency to decrease glyphosate sorption (Gimsing et al., 2004b). Generally, at high soil pH (>7), the proportion of negatively-charged soil colloids increases and glyphosate molecules exist as HG^{2-} (~100%, Munira et al., 2016). It has also been shown that water soluble humic substances found in soil solution can facilitate glyphosate leaching to lower soil layers (Piccolo et al., 1994).

It is therefore clear that a number of soil characteristics influence the bioavailability and transport of glyphosate residues in soil. To date, there has been a focus on predicting glyphosate fate and availability through empirical and mechanistic modelling, with varying success (Barrett and McBride, 2007; Glass, 1987; Gimsing et al., 2004b). However, direct assessment of glyphosate bioavailability to date has been limited, due to a lack of an appropriate methodology. Current analytical methods generally aim to measure total residue loads, through exhaustive extraction with or without correction for recovery by spiking with internally-labelled isotopic standards (Botero-Coy et al., 2013; Koskinen et al., 2016). A key limitation in assessing the bioavailable glyphosate lies in the small volume of pore water in soil and the low amount of glyphosate remaining in the pore water (Vereecken, 2005). A potential solution to this is the application of diffusive gradient in thin-films (DGT), an analytical technique that measures the diffusive supply of elements and compounds by acting as an infinite sink (Degryse et al., 2009). The technique differs from other extraction techniques by responding to kinetics of release from the soil rather than relying on a pseudo-equilibrium between extractant and soil, so that the analyte present in the soil solution and the fraction resupplied from the solid phase are measured. As such, DGT has been shown to effectively predict plant-available P (Tandy et al., 2011). DGT has been identified as a valid passive sampling technique for total glyphosate in aquatic environments (Fauvelle et al., 2015), but as far as we are aware, the potential for DGT to effectively assess bioavailable glyphosate across different soil types has not yet been tested.

A number of potential challenges may arise in applying DGT in the assessment of bioavailable glyphosate in soil. The competition of common soil anions, especially phosphate (Tandy et al., 2011; Mason et al., 2010) with glyphosate for the DGT binding layer, could provide a misleading account of the true glyphosate availability.

To address these questions, we aimed to establish the boundary conditions for the use of DGT with glyphosate and to test the potential for the DGT technique to quantify glyphosate availability in different soils. We hypothesize that DGT-available glyphosate will provide a useful estimate of plant available glyphosate than currently available analytical methods. This was tested by spiking four soils, differing in their capacity to bind/fix glyphosate, with a range of glyphosate concentrations and concurrently measuring root growth inhibition of two different plant species, wheat (*Triticum aestivum*) and narrowleaf lupin (*Lupinus angustifolius*).

2. Material and methods

The overall experimental design is shown in Fig. 1.

2.1. Soil characterisation

Four contrasting soils were used for these experiments. Soils were taken from Australian grain cropping fields from locations shown in Table 1. The soils were air-dried, sieved to <2 mm, and stored in sealed containers at ambient temperature until use. Soil properties were measured on all soils: pH (1:5 0.01 M $CaCl_2$), plant available P (Colwell P), texture, total organic C content, calcium carbonate content, maximum water holding capacity, CEC at soil pH, and exchangeable cations, using methods described in Rayment and Lyons (2010). The physicochemical characteristics and glyphosate residue concentration of each soil are given in Table 1.

Soils were further characterized by X-ray diffraction (XRD) and mid-infra-red (MIR) reflectance spectrometry. X-ray diffraction (XRD) patterns were collected using a Bruker D8 Advance Diffractometer, operating at 40 kV with a copper lamp. Scans were collected between 5° and 70° in steps of 0.019°. Qualitative assessment of the diffraction patterns was conducted using DIFFRAC-EVA. Mid-infrared (MIR) analysis of the soils for predictions of particle size and mineralogy were conducted with VIC-DGET using the method and model outlined in the literature (Robinson and Kitching, 2016). All soils were air dried and ground with a mortar and pestle to a fine homogenous texture prior to analysis.

2.2. DGT boundary conditions: effect of pH, P and bicarbonate on DGT accumulation of glyphosate

2.2.1. Experimental setup

The effect of different solution chemistries (pH, phosphate and bicarbonate concentrations) on glyphosate accumulation by DGT was tested to assess the boundary conditions of this technique. Elution recovery of glyphosate for the DGT was measured using a published method (Fauvelle et al., 2015). In brief, three polypropylene tubes were filled with 12 mL of 1 ng mL^{-1} ^{14}C-labeled glyphosate (specific activity 7.5 kBq L^{-1}; 95% purity, American Radiolabeled Chemicals, Saint