Assessment of the Diffusive Gradients in Thin-films (DGT) technique to assess the plant availability of Mn in soils

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Abstract

Problems with Mn deficiency are significant in global crop production. Attempts to assess Mn availability have been impeded as Mn is highly redox reactive and can be present in soil in a variety of species having very different availability and behaviour depending on soil conditions. The Diffusive Gradients in Thin-films (DGT) technique is one of the most promising techniques for assessing nutrient and contaminant availability in soils. However, the use of the DGT to assess Mn has never been fully validated. Here we present a series of experiments validating the DGT technique for Mn in soil. Furthermore, by coupling DGT with X-ray absorption spectroscopy (XANES) we provide an insight into the soil factors controlling Mn speciation and availability in soil.

Key Words

Manganese, soil, DGT, availability, XANES.

Introduction

Problems with Mn deficiency are significant in global crop production, occurring under a range of different soil- and climatic conditions, though it is said to be most prevalent in cool temperate regions (Reuter *et al.* 1988). For instance, in Denmark Mn deficiencies have increased for reasons not yet completely understood, and today Mn deficiency is the most important nutritional disorder in the production of cereals (Hebbern *et al.* 2005).

Mn in soils is generally found in three different oxidation states – Mn(II), Mn(III), and Mn(IV). Plant roots take up mainly Mn(II). Acidic soils favour the presence of Mn(II) while oxidizing and alkaline soils would favour the presence of precipitated Mn(III) and Mn(IV) oxides (Norvell 1988). Attempts to assess Mn availability have been impeded due to the high reactivity of Mn to differences in soil conditions. For instance drying and wetting of soils will influence the Mn availability. Often flooding of soils will lead to reduction of Mn(III) and Mn(IV) resulting in an increase in the Mn(II) concentration in the soil solution; consequently Mn deficiency in lowland flooded rice is very uncommon. Drying of soils will on the other hand lead to oxidation of Mn(II), which will then precipitate as oxides and limit availability (Reuter *et al.* 1988).

When assessing the plant availability of nutrients, extractions with chelating agents or neutral salts are generally used (Menzies *et al.* 2007; Rao *et al.* 2008). However the applicability of these techniques under a variety of different soil- and environmental conditions has been questioned. This is particular relevant for elements, such as Mn, which are redox sensitive and can be present in soil in a variety of chemical species having very different plant availability and behaviour. As an alternative, Davison *et al.* (2007) and Zhang and Davison (2006) have proposed the use of the Diffusive Gradients in Thin-films (DGT) technique. We have evaluated the possibility of measuring Mn availability with DGTs under a variety of different soil conditions, including different redox conditions.

Methods

To test whether DGT can be used to assess Mn status of soils we tested the DGTs in solutions and soils under a variety of conditions relevant to agricultural conditions.

1) DGTs were deployed in solutions at three pH values (4, 5, and 6). For each pH value three Mn concentrations (5, 50, and 100 µg/l) were tested.

2) The impact of potentially competing cations for binding to the DGT resin was analysed by varying the concentrations of Mg, Ca, and Fe. Model soil solutions were prepared with 50 µg/l Mn, with a pH of 6.5. Three different solutions were prepared with different concentrations of Ca (50, 500, and 1000 mg/l) Mg (5, 50, and 100 mg/l) and Fe(II) (50, 500, and 5000 µg/l). These were chosen to represent low medium and high soil solution concentrations of Ca, Mg, and Fe. The whole experiment was conducted in a glove-box under anaerobic conditions so that Fe(II) could be kept in solution.

3) To analyse if measurements of Mn plant availability were compromised by differences in deployment time, DGTs were deployed in 3 different soils, previously characterised as having low-, medium-, and high-Mn availability, respectively. For all soils DGTs were deployed for periods of 0.5, 1, 2, 3 and 6 days after the water holding capacity (WHC) of the soils had been adjusted to 100 %.

4) Finally an experiment was conducted to evaluate if the DGT could also be used to mimic the changes in Mn plant availability caused by changes in redox potential. This was done by deploying DGTs in the same three soils as described above. This time DGTs were deployed for 1, 5, or 10 days under anaerobic conditions. For all soils and all deployment times there was a treatment with and one without glucose addition. The glucose was added to induce marked redox changes. For comparison, DGTs were also deployed for 1 day under aerobic conditions and without glucose addition. Instead of deploying the DGTs in larger soil samples, as it is normally done for DGTs, we smeared the wet soil on the DGT surface in a thin layer (1.15mm ± 0.03mm) so that the DGT would be able to deplete the Mn in the soil. The soil samples were then analysed at a synchrotron facility (MaxII, MaxLab, Lund University, Sweden) to get information on the Mn speciation. The X-ray Absorption Near Eedge Spectroscopy (XANES) results were then compared with those of soils that had not been depleted by DGTs.

Results
The results of the first model solution experiment showed that for all concentrations tested the DGT device was able to accurately predict the Mn solution concentration at pH 4, 5, and 6. The difference between the solution concentration and the DGT predicted concentration was, for all pH values and at all concentration, 10% or lower.

The results from the second solution experiment showed that DGTs were able to absorb Mn in the presence of competing cations. However, there was a slight but significant decrease in the amount of Mn adsorbed as the concentration of competing cations increased. More detailed work will have to be conducted to precisely establish the conditions under which the ability of assessing Mn availability is affected. Both in regards to the concentrations of the competing cations, but also for pH as it is likely that the competition might be further increased at lower pH values. However, we would not expect this to be a great problem in an average agricultural soil where concentrations of competing cations are expected to be lower than the critical values used in this experiment.

There was no difference between soil deployment times from 12 hours up to 3 days for the soils having low and medium Mn levels. However, after 6 days the Mn levels increased significantly. For the soil with the highest Mn status the DGT measurements of Mn availability were only stable for the first 2 days. Already at day 3 the DGT-Mn was doubled, and at day 6 the Mn level was had almost doubled again. These results correspond with measurements of the soil redox potential.

The result from the experiment where the DGTs were deployed at different periods of time in an anaerobic cabinet showed that the availability of Mn increased significantly when soils were kept anaerobic compared to aerobic controls. For the soil with low Mn status there was the largest effect of the added glucose. This meant that with the addition of glucose the amount of available Mn increased significantly, reaching levels similar to the soil with the highest Mn status. For the other two soils there were no, or only small, effects of the added glucose. . This could indicate that the low Mn availability is related to a carbon limitation more than to an actual limitation in the amount of Mn.
When comparing soils that had been exposed to DGTs with soils that had not, by XANES analysis it is clear that the DGT devices deplete the soils of Mn(II), which is also the predominant form available to plant roots (Figure 1).
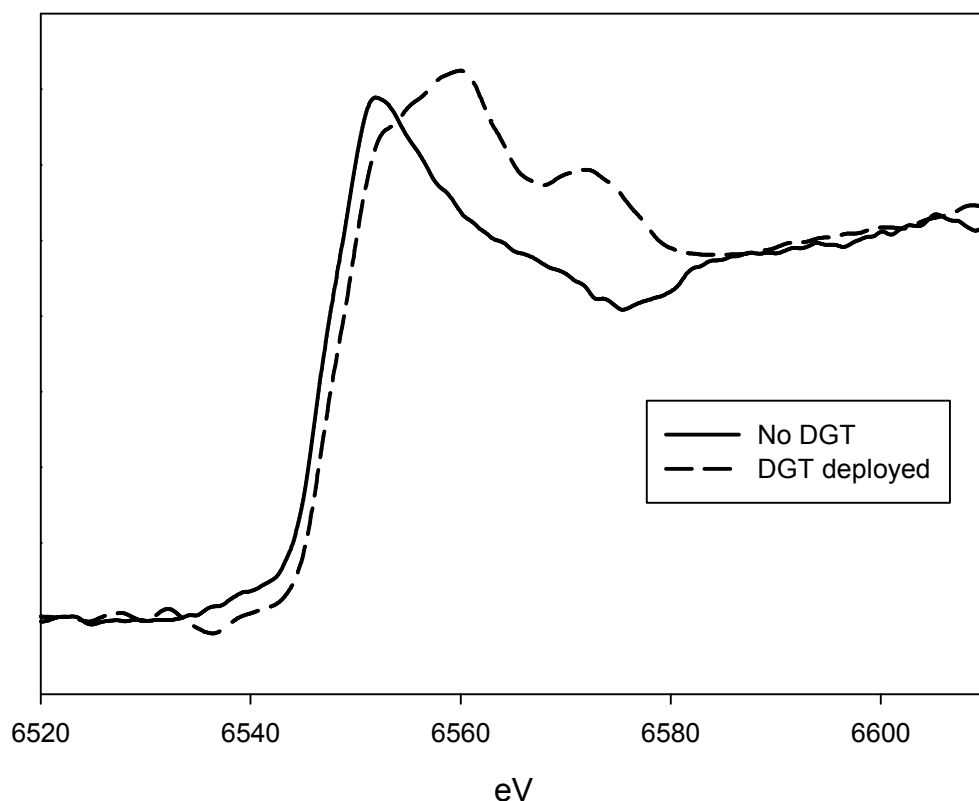
Figure 1. Mn K-edge XANES of the high available soil after 1 day of incubation. The No DGT spectrum refer to the soil not subject to DGT deployment, the dashed line refers to the same soil after DGT deployment. It is evident that the proportion of oxidised forms of Mn (characterised by an higher absorption edge) is larger in the DGT deployed soil. This indicates that DGT has depleted the reduced Mn pool.

Conclusion

The results of this series of experiment assessed the boundary conditions and the mechanisms of Mn uptake by the DGT devices. The results are in line with expectations and indicate that DGT provides an insight into the understanding of Mn availability as related to changes in speciation. The next step will be the development of a protocol able to identify soils prone to Mn deficiency.

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