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Title

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

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Introduction.

Manganese (Mn) was proposed as an essential plant nutrient in 1905 by Bertrand (Bertrand, 1905; Eyster et al., 1958). 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). 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), which is the predominant form in solution or on the exchangeable sites of soil particles. In solution Mn(II) is found either as the Mn^{2+} cation or in complexes with inorganic or organic ligands. 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). Apart from soil conditions microorganisms play a great role in the processes of reduction and oxidation of Mn.

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 particularly 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.

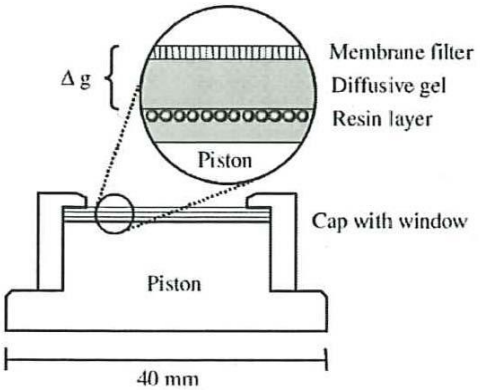

Figure 1: Cross section of the DGT device showing the membrane filter on top of the diffusive gel and the resin gel with the chelex on one side. All held together by the holder consisting of the piston and the cap with an exposure window (Dahlqvist et al., 2002).

The principle of the DGT is to mimic the uptake of nutrients by plants by also acting as an infinite sink. Especially for metals this has so far given new insights into the assessment of plant availability of nutrients (Sonmez and Pierzynski, 2005; Zhang et al., 2001; Zhao et al., 2006). The DGT works by having a binding gel placed behind a diffusive gel with a known diffusion

coefficient (Figure 1). The binding gel adsorbs the given nutrient causing a concentration gradient over the diffusive gel and nutrients will then move down the concentration gradient causing a flux of nutrients, which can be calculated based on the amount of nutrients adsorbed (Figure 2).

DGT, designed in the mid 90's to assess trace elements in seawater (Davison and Zhang, 1994; Zhang and Davison, 1995), is recognised as one of the most promising techniques to assess availability of nutrients and contaminants in soil (Davison et al., 2007). We have evaluated the possibility of measuring Mn availability with DGTs under a variety of different soil conditions, including different redox conditions.

Material and Methods.

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

1) DGTs were deployed in solutions with pH values adjusted to 4, 5, and 6. For each pH value three Mn concentrations (5, 50, and 100 µg L^{-1}) were tested to assess whether the DGT would adsorb Mn under different pH conditions likely to occur in soil.

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^{-1}Mn to represent a medium Mn soil with pH 6.5. Three different solutions were prepared with different concentrations of Ca (50, 500, and 1000 mg L^{-1}), Mg (5, 50, and 100 mg L^{-1}), and Fe(II) (50, 500, and 5000 µg L^{-1}). These were chosen to represent low, medium, and high soil solution concentrations of Ca, Mg, and Fe. Before deployment the solutions were sampled to determine the exact Mn concentrations. 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 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. For all soils DGTs were deployed for periods of 12 hours, 1 day, 2 days, 3 days, and 6 days after the water holding capacity (WHC) of the soils had been adjusted to 100 % (and the soils left for 24 hours to equilibrate). This is compared to the standard protocol, which prescribes a 24 hour deployment of the DGT devices.

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 were treatments with and 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, 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.

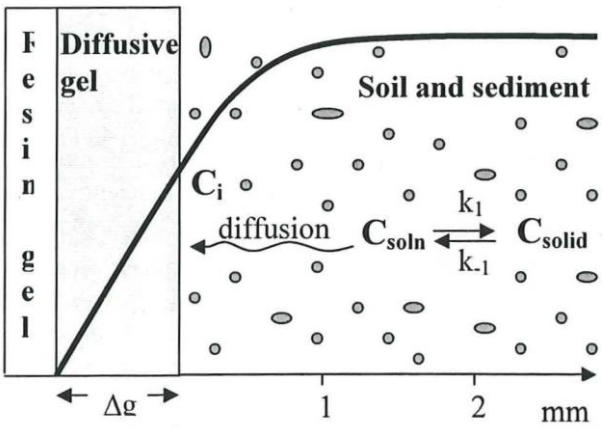

Figure 2: Schematic representation of the concentration gradient through a DGT device and the adjacent soil. C_{soln} and C_{solid} represents the concentration in the solution and solid phase respectively. C_i (referred to as C_{DGT} in the text) is the concentration at the interphase between the DGT device and the soil (the membrane filter is not shown in the figure).(Davison et al., 2007).

Figure 2 presents the theoretical background for the following calculations. As the resin acts as an infinite sink the concentration at the interface between the resin gel and the diffusive gel will be zero. With a known concentration gradient in the diffusive gel we can calculate the flux through the diffusive gel and the C_{DGT} (C_i in Figure 2), which represents the mean Mn concentration at the surface of the DGT unit.
The flux (F) of nutrients into the binding layer of the gel is calculated by:

$$F = \frac{M}{tA}$$

where M is the mass of nutrients and A is the area of the exposure window of the DGT, while t is the time of deployment. By using the flux we can then calculate $C_{DGT:}$

$$C_{DGT} = \frac{F\Delta g}{D}$$

where Δg is the thickness of the diffusive layer (filter membrane + diffusive gel) and D is the diffusion coefficient in the gel.

Results.

The results of the first model solution experiment showed that for all concentrations tested (5, 50, and 100 µg L^{-1}Mn) the DGT device was able to accurately predict the Mn solution concentration at pH 4, 5, and 6. Differences between solution concentrations and DGT predicted concentrations were 10% or lower for all pH values and at all concentration (data not shown).

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 decrease in the amount of Mn adsorbed as the concentration of competing cations increased.

Table 1: Mn concentrations in solution and DGT measurements with SE (n = 3) at pH 6.5. Concentrations of competing cations were 50, 500 and 1000 mg L^{-1} for Ca and 5, 50 and 100 mg L^{-1} for Mg, and 50, 500, and 5000 µg L^{-1} for Fe. The three concentrations were selected to represent low, medium and high concentrations respectively.

pH	competing cations	Mn concentraton (µg L^{-1})	SE	C_{DGT} (µg L^{-1})	SE
6.5	low	39.19	0.72	47.28	1.59
6.5	medium	38.34	0.51	40.10	0.60
6.5	high	36.93	0.12	30.45	1.53

From the DGT deployments in soil the Mn measurements are expressed below as C_{DGT}. The results indicate that 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 (Figure 3). 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 C_{DGT} was doubled, and at day 6 the Mn level had almost doubled again. The data for the first and last deployment times are reported in Figure 3. These results correspond with measurements of the soil redox potential (data not shown). For the two soils with the lowest Mn status reduction happened mainly after 6 days while the reduction could be measured already after 2 days in the soil with the highest Mn status.

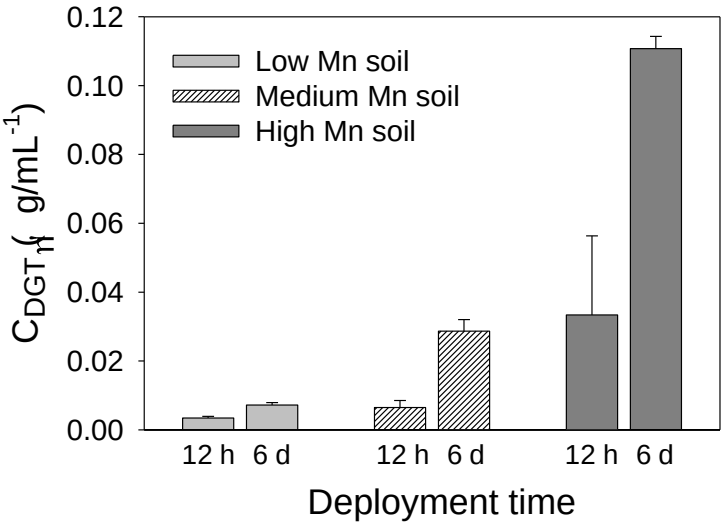

Figure 3: Mn availability and SE (n = 3) measured with DGTs after 12 hours or 6 days of deployment in three soils with different Mn levels.

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. Also the Mn levels were significantly higher than compared to the levels measured under aerobic conditions in the first experiment (Figure 3). 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 (Figure 4). For the other two soils there were no, or only small, effects of the added glucose.

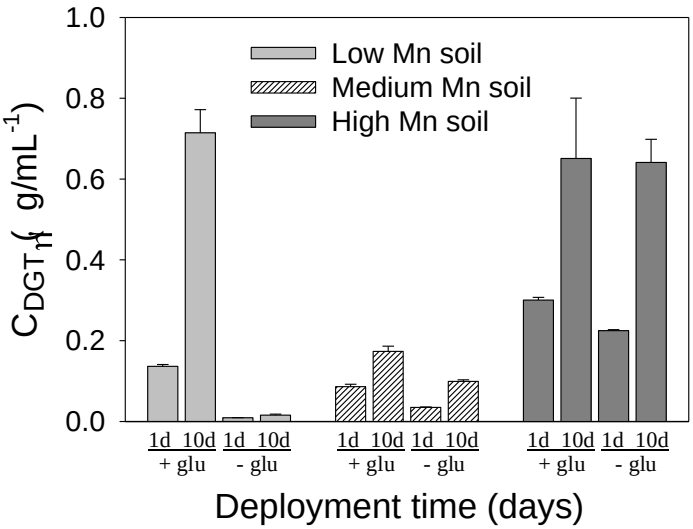

Figure 4: Mn availability and SE (n = 3) measured with DGTs after 1 and 10 days of deployment in three different soils either with or without the addition of glucose (+glu or –glu). All handling was undertaken in an anaerobic cabinet.

The change in redox status, and the consequent reduction of Mn when the soils were kept under anaerobic conditions were confirmed by the Mn XANES spectra. With increasing anaerobic incubation time the Mn K-edge and white lines were shifted to lower energy, indicating a progressive reduction of Mn oxides. Also, the Mn XANES analysis of the soils deployed and not deployed by DGT showed clear differences in Mn speciation. After deployment of the DGT, the proportion of Mn(II) was significantly lower and the proportion of Mn(III) and Mn(IV) was significantly higher than when the soil had not been exposed to DGTs. This result clearly demonstrate that the DGT device, similar to a plant root, depletes the Mn(II) pool in soil.

Discussion.

The model soil solution experiments were conducted to test the validity of using DGTs to assess the Mn status in soils. The first test, where we measured Mn in a solution with different concentrations of Mn and at different pH levels, showed that DGT can be used to very accurately predict the Mn concentrations in solutions at various pH values. It is expected that since the DGT worked at pH 4 to 6 it will also work at higher pH values where less proton competition is expected.

The experiment with competing cations showed that for a range of Ca, Mg, and Fe concentrations relevant for the soil solution it was possible to measure the Mn concentration accurately (Table 1). However, the results indicated that as the concentrations of competing cations increased this had a negative effect on the ability of the DGT to adsorb Mn. 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.

As the calculation of C_{DGT} takes into account the deployment time, C_{DGT} would stay constant over time if the supply of Mn is constant. For the first 2 to 3 days it was observed that the amount of Mn

adsorbed was constant for the different soils. After this period, Mn was reduced and the plant availability measured by the DGTs increased significantly (Figure 3). This result is in agreement with the decrease in redox potential that was observed over time, and corresponds well with the expectation that a near saturated soil, after a certain period of time, will release Mn due to reduction. The differences between the soils highlight the importance of considering both soil properties as well as soil conditions when determining Mn availability.

From the results in Figure 4 it was clearly shown that the plant availability of Mn was increased by the anaerobic deployment, which is in agreement with the finding that a reduction of Mn(III) and Mn(IV) should occur under anoxic conditions. This also confirms that total Mn is not a reliable indicator of Mn plant availability. The fundamental role of the redox potential in controlling Mn solubility is clearly shown by the addition of glucose, which resulted in a significant increase in Mn availability in the soil categorized as having the lowest Mn status. After the addition of glucose, the Mn availability was significantly higher than in the medium soil and as high as in the high-Mn soil. 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. The Mn XANES spectra provided a good correlation between the proportion of Mn(II) and the amount of Mn adsorbed by the DGTs.

Conclusion.

From our results it can be concluded that the DGT technique has potential for assessing plant availability of Mn for a range of conditions relevant to agricultural soils. However, in future studies, plant tests should be conducted to assess the correlation between DGT predicted Mn concentrations and plant tissue concentrations. Our results showed that the DGT technique when combined with redox experiments is an efficient method to analyse if a soil is prone to be Mn deficient or not. Furthermore, this technique can be used to assess the likely mechanism controlling Mn availability in soil (e.g. redox potential, C limitations etc.).

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