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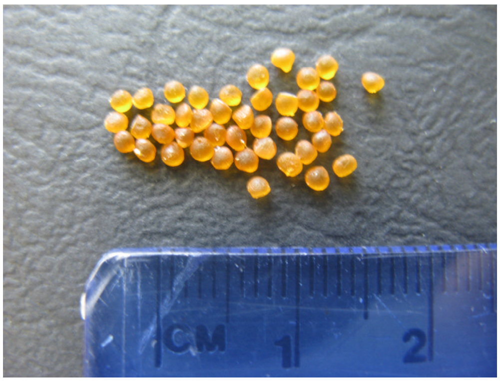
New biodegradable hydrogel materials for the delivery of nitrification and urease inhibitors



Biodegradable hydrogel beads containing DCD

Key external stakeholders:

All farmers, Department of Agriculture, Food & Marine, Environmental Protection Agency, Industry

Practical implications for stakeholders:

Dicyandiamide (DCD) is an effective nitrification inhibitor that reduces nitrate production in soil and associated environmental losses of nitrogen, and increases nitrogen use efficiency. The efficacy of DCD is variable in soil and this has been linked to leaching and microbial degradation of DCD from soil. Hydrogels provide a slow release mechanism that could improve the efficacy of DCD released in soil and improve its efficacy as a tool to increase the utilisation of nitrogen in soil.

- **Farmers:** Hydrogels are a viable potential tool to improve the efficacy of DCD by prolonging its presence in soil.
- **Policymakers:** DCD is an effective nitrification inhibitor but it degrades in soils at different rates. Hydrogels slowly release DCD from a protective biodegradable porous matrix.
- **Scientific:** DCD degradation is a soil specific process that relates to soil chemical and microbial properties. Hydrogels slow DCD release and this could be a potential tool to increase DCD efficacy.

Main results:

- Soil type had a significant effect on the breakdown of DCD over time and this could result in reduced efficacy when DCD degrades quickly in soil.
- For DCD to efficiently mitigate N losses to the environment, soil type specific application timings and rates need to be established.
- Alternatively, the use of a chitosan hydrogel has shown some potential to slowly release DCD in soil under moderate moisture conditions, but more research is needed to improve this new technology.

Opportunity / Benefit:

- Chitosan hydrogel is a potential tool for increasing the efficacy of DCD on nitrification in soil.

Collaborating Institutions:

NUI Maynooth

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Dr. Eddy Minet
External collaborators: Dr. Denise Rooney, Prof. Carmel Breslin (NUI Maynooth)

1. Project background:

Reactive nitrogen (N) losses and greenhouse gas emissions from agricultural soils are a source of concern for animal/human health and the environment. To mitigate agriculture's environmental footprint, a commercially available nitrification inhibitor dicyandiamide (DCD) has been used with some success to slow down NO3- production and reduce N2O emissions. However, inhibitors have a limited life-span in soils and repeated applications are required to maintain efficiency. The objective of this research was i) to estimate the impact of DCD degradation on nitrification inhibition across soils with contrasting physical and chemical characteristics, and ii) to test the potential of an alternative application method whereby inhibitor DCD is encapsulated in a protective slow-release matrix of biodegradable polymeric hydrogel.

2. Questions addressed by the project:

This research addressed the following questions:

- What are the factors driving DCD degradation in soil?
- How does DCD degradation impact nitrification inhibition in soil?
- Can the encapsulation of DCD in slow-release chitosan hydrogel be a viable method of DCD field application (as opposed to repeated spray applications)?

3. The experimental studies:

The impact of DCD degradation was studied on twenty-one soil types (Ireland and UK) that received two treatments: 20 kg/ha NH4-N ± DCD (15 kg/ha DCD). Soil units arranged in a randomised block design were incubated in triplicate at 15°C for 6 times (between 2 days and 64 days). Samples were then extracted with 2M KCl and analysed for DCD (HPLC analysis) and NO3-N content (colorimetry). Based on these measurements, two response variables were calculated: DCD degradation constant (from an exponential decay model) and % nitrification inhibition. Regression analysis was carried out for each incubation time. Chitosan hydrogel beads were formed by precipitation of a chitosan gelling solution and covalent crosslinking with glyoxal (excess glyoxal was partly removed (C beads) or allowed to polymerise upon drying (CG beads)). Slow-release of DCD was tested with twenty beads dropped on compacted soil (equivalent to 15 kg DCD/ha). The experiment was conducted investigating the effect of time, rainfall, soil moisture (expressed as % of water holding capacity (WHC)) and partial removal of excess glyoxal from the beads.

4. Main results:

Soils used in the first part of the experiment (DCD degradation) contained between 0.89 and 9.4 % organic C. % sand, silt and clay ranged between 21 and 68, 20 and 51, 11 and 30, respectively. Soil pH varied between 4.6 and 7.6. DCD degradation was equally variable. A 24% DCD loss was observed after 64 days from the soil with the lowest constant k (1.8), whereas a 93% DCD loss was observed from the soil with the highest k (18.8). For most soils, % nitrification inhibition increased sharply until incubation day 8 or 16 and stabilised or slightly decreased thereafter. There was a significant ($p < 0.05$, day 64 not significant) negative correlation between DCD degradation constant k and % nitrification inhibition. In other words, the higher the degradation rate of DCD, the lower the % nitrification inhibition. These results suggest that some soils with faster DCD degradation will possibly require more frequent/higher rates of application. This could be dealt with more conveniently (and possibly more efficiently) if small amounts of DCD were consistently delivered over long periods of time.

In the second part of the study, the incubation of beads in soil resulted in a delayed release of DCD. DCD soil release significantly increased with time ($p \leq 0.0001$). Treatment also had a significant effect ($p \leq 0.0001$): rainfall caused more DCD release than soil moisture (WHC). Finally, higher rates of rainfall or WHC significantly ($p \leq 0.0001$) increased DCD bead release. After seven days, incubation of C beads caused the release of 74 to 98% of the total DCD bead content. Some of the DCD remaining in the beads has been shown to be more durably trapped inside the beads. In comparison with the C beads (219 µg DCD loaded per bead), CG beads contained less DCD (43 µg DCD per bead), but DCD release was much slower (33 % of total DCD bead content released after seven days under high rainfall conditions). These results suggest that a combination of C and CG beads could be used to fit two purposes: a quick release of DCD with C beads necessary after fertiliser (urea or ammonium based) or slurry application, and a slower release of DCD with CG beads to sustain nitrification inhibition.

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5. Opportunity/Benefit:

Soil properties affect the efficacy of DCD on nitrification and this relates to DCD degradation. Chitosan beads are a viable method to reduce DCD release rate in soil and increase its efficacy on nitrification.

6. Dissemination:

The results of the project have been presented at national and international conferences. There is one scientific paper published and a number of other papers in preparation. The outputs from the project have been sent to relevant national policy makers.

Main publications:

Minet E.P., O'Carroll C., Rooney D., Beslin C, McCarthy C.P., Gallagher L. and Richards K.G. (2013) Slow delivery of a nitrification inhibitor (dicyandiamide) to soil using a biodegradable hydrogel of chitosan. Chemosphere In Press.

Minet E., Richards K.G., Rooney D., Breslin C., O'Carroll C. and Gallagher L. (2012) Slow delivery of nitrification inhibitor to soil using a biodegradable hydrogel: testing of a novel approach to mitigate N losses and GHG emissions, Agricultural Research Forum Tullamore, Ireland, 12-13 March 2012, p.13.

Popular publications:

Richards, K.G., Selbie, D., Cahalan, E., Dennis, S., Ernfors, M., Minet, E., Lanigan, Gary, Lalor, S., Murphy, J.B., Watson, C., Laughlin, R., McGeough, K., Mueller, C., Rooney, D., Cameron, K., Di, H., Khalil, I. and Hennessy, D. (2011). Reducing N loss using inhibitors. Tresearch 6 (2) p. 12-13 (Summer 2011)

7. Compiled by: Dr. Karl Richards

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