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Mustard catch crop enhances denitrification in shallow groundwater beneath a spring barley field

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HIGHLIGHTS

- Mustard cover crop after spring barley enhances groundwater denitrification.
- Mustard increases dissolved organic carbon (DOC) in shallow groundwater.
- Denitrification in shallow groundwater is an *in situ* process.
- Denitrification below mustard system results in mainly N_2.
- Without mustard, groundwater denitrification below spring barley produces only N_2O.

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ABSTRACT

Over-winter green cover crops have been reported to increase dissolved organic carbon (DOC) concentrations in groundwater, which can be used as an energy source for denitrifiers. This study investigates the impact of a mustard catch crop on *in situ* denitrification and nitrous oxide (N_2O) emissions from an aquifer overlain by arable land. Denitrification rates and N_2O-N/(N_2O-N + N_2-N) mole fractions were measured *in situ* with a push–pull method in shallow groundwater under a spring barley system in experimental plots with and without a mustard cover crop. The results suggest that a mustard cover crop could substantially enhance reduction of groundwater nitrate (NO_3^--N) via denitrification without significantly increasing N_2O emissions. Mean total denitrification (TDN) rates below mustard cover crop and no cover crop were 7.61 and 0.002 μg kg^{-1} d^{-1}, respectively. Estimated N_2O-N/(N_2O-N + N_2-N) ratios, being 0.001 and 1.0 below mustard cover crop and no cover crop respectively, indicate that denitrification below mustard cover crop reduces N_2O to N_2, unlike the plot with no cover crop. The observed enhanced denitrification under the mustard cover crop may result from the higher groundwater DOC under mustard cover crop (1.53 mg L^{-1}) than no cover crop (0.90 mg L^{-1}) being added by the root exudates and root masses of mustard. This study gives insights into the missing piece in agricultural nitrogen (N) balance and groundwater derived N_2O emissions under arable land and thus helps minimise the uncertainty in agricultural N and N_2O-N balances.

1. Introduction

Groundwater contamination by NO_3^--N is a cause of concern for the environment (Galloway et al., 2008). Aquifer discharge of NO_3^--N into streams, lakes, rivers and coastal transitional waters can increase the risk of eutrophication in surface waters (Stark and Richards, 2008). Excessive NO_3^--N leaching to groundwater below arable land in a spring barley system, where land is left fallow over winter, has been reported before by Hooker et al. (2008). In tillage farming, cover crops reduce NO_3^--N leaching to groundwater through the uptake of N during the fallow period between crop harvest and subsequent planting of the next crop (Shepherd et al., 1993). Over a three years period mustard sown has been found to reduce mean groundwater NO_3^--N concentration by c. 25% (Premrov et al., 2012). The mean DOC concentrations were found to be significantly higher by c. 32% under the mustard cover crop than under no cover crop, suggesting that mustard may help reduce groundwater NO_3^--N occurrence by (i) taking up soil N and/or supplying DOC in groundwater to enhance denitrification.

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Nitrate reduction into un-reactive N via denitrification can be accompanied by the emissions of N_2O, a potent greenhouse gas with global warming potential of 298 (IPCC, 2007). The contribution of the leached NO_3^--N with associated groundwater to indirect N_2O-N emissions is well recognised (IPCC, 2007) but the dynamics of N_2O production and reduction *in situ* in groundwater is not yet well understood (Clough et al., 2007). Moreover, in measuring denitrification in groundwater, it is often unclear if denitrification products are produced *in situ* or if they have been leached from surface soils (Groffman et al., 1998). An estimation of N_2O-N/(N_2O-N + N_2-N)) ratios is necessary to know the potential of pollution swapping for NO_3^--N to N_2O-N. Moreover, quantification of the end product of denitrification, N_2-N, is also important to minimise uncertainty in the agricultural N balance (Galloway et al., 2004).

While previous research recognised the importance of mustard as an over winter cover crop in reducing NO_3^--N leaching to groundwater during the winter recharge (Hooker et al., 2008; Premrov et al., 2012), there are no reports on the effect of cover crops on groundwater denitrification and the N_2O or N_2 transformation rates. This information is crucial to better understand N cycling below an arable system and to improve land management. The objective of this experiment was to investigate the effect of a mustard cover crop on *in situ* denitrification rates and N_2O-N/(N_2O-N + N_2-N) ratios in shallow groundwater under a spring barley cropping system.

2. Methodology

2.1. Site and experimental design

The experiment was carried out during February–March, 2011 at Oak park Research Centre, Co. Carlow, Ireland (52°51′43″N, 6°54′53″W) in a shallow sand/gravel aquifer (water table <2.5 m below ground level, bgl). The top soil is a well drained sandy loam overlying inter-bedded layers of sand, gravel and silt/clay. The shallow fluvioglacial sand and gravel aquifer is underlain by a deeper Carboniferous limestone aquifer. Two over winter treatments within a spring barley system have been cultivated since 2006: (1) mustard cover crop and (2) no cover crop, as part of a larger experiment on the effect of over winter green cover on NO_3^--N leaching. Three independent piezometers (PVC pipe; 0.03 m i.d. and 1.0 m screen section) were installed in each treatment to a depth of 4 m bgl. The treatment plots were oriented to the dominant groundwater flow to ensure hydrogeological homogeneity and to minimise lateral flow. Leaching is the dominant hydrological pathway as overland flow on this site was considered negligible due to the free draining nature of soils and subsoils. Inorganic N fertiliser "Super Nett" (27% N and 3.7% S) and KCl were used at a rate ranged from 115–135 kg N and 35–91 kg Cl ha^{-1}. Spring barley was grown during March to August. Mustard cover crop was grown during November to April and incorporated into the soil by ploughing with chisel prior to the next barley cropping.

2.2. In situ push–pull method

Denitrification rates in groundwater were measured *in situ* using a push-pull method described by Addy et al. (2002). In brief, the push–pull method consists of collecting groundwater from a well, amending it with ^{15}N-enriched NO_3^--N and a conservative tracer (bromide), injecting the solution in the aquifer ("push"), incubating for 4-h and pumping back ("pull"). Ten L of groundwater (fill 43.4 kg of aquifer materials; bulk density: 1.65 g cm^{-3}; porosity: 38%) was collected from each well (depth 4 m bgl) in a plastic container (carboy) using a peristaltic pump (Model 410, Solinst Canada Ltd.) and immediately enriched with 50 mg L^{-1} Br^- (as KBr) and 50 mg L^{-1} isotopically enriched (50 atom% ^{15}N) NO_3^--N (as KNO_3^--N). The dosing solutions (i.e., the 10 L of amended groundwater) were pushed into the wells (4 m bgl) at a low rate (15 L h^{-1}) with a peristaltic pump to minimise changes in the hydraulic potential surrounding the well. To ensure that the DO content of the enriched solution is same to the collected groundwater, DO was monitored using a probe (Multi 340i/SET, WTW, Germany). A small quantity of the dosing solution (targeted 500 mL) was left at the bottom of the carboy to measure dissolved gases and hydrochemistry.

Incubation time was set at 4 h because previous study on this site indicated that longer or shorter than 4 h incubations can respectively, reduce recovery of injected solution or detection of denitrification products (Jahangir et al., 2013a). After incubation for 4 h, 20 L of groundwater was pulled from each well at the same rate (15 L h^{-1}) as during the push phase to avoid generating gas bubbles within the gas-impermeable Teflon tubing. Groundwater samples were collected at 2 L intervals into 160 mL glass serum bottles for dissolved N_2O-N and N_2-N analysis and into 50 mL plastic tubes for the measurement of hydrochemical parameters. The Teflon outlet was placed at the bottom of the glass bottle, gradually filled with groundwater and immediately sealed with butyl rubber septa and aluminium crimp caps (Wheaton, USA). No visible air bubbles were observed in the sample. In a preliminary test, such samples taken directly in the glass bottles; or indirectly using a syringe attached to an air-tight sampling tube (Teflon) connected to the outlet of the pump did not show any significant differences in dissolved N_2O, CO_2 and CH_4 concentrations. All samples were submerged under water in a polystyrene box and stored at 4 °C until analysed for dissolved gases, ions and hydrochemistry within one week of collection.

2.3. Dissolved gases and hydrochemical analyses

Denitrification products in groundwater (N_2O-N and N_2-N) were extracted using the phase equilibration headspace extraction technique (Davidson and Firestone, 1988) with helium (*He*; BOC, Linde Group, Germany) filling the headspace (*He*: water 3:1; v/v). In brief, samples in the serum bottles were shaken for 13 min on a Gyrotory shaker (Model G-10, New Brunswick Scientific Co., USA) and left for a standing period of 63 min (Jahangir et al., 2012b). Headspace samples were then taken in 12 mL exetainers (Labco Inc. Wycomb, UK) using a syringe after injecting additional 15 mL of high purity *He* for the analysis of N_2O and N_2 concentrations and the ^{15}N enrichment of N_2O and N_2. Concentrations and isotopic composition of N_2O-N and N_2-N were determined on a dual-inlet isotope ratio mass spectrometer (Stable Isotope Facility, UC Davis, CA) as described by Mosier and Schimel (1993).

Dissolved N_2O-N and N_2-N concentrations were calculated using the three highest recovery values (plume core; being estimated from the recovery of tracer in the pulled water) within sample replicates (Harrison et al., 2011) to minimise the effects of uncertainty of estimation due to physical attenuation. For each piezometer, conservative tracer (Br^-) recovery was estimated as C/C_0; where C was the tracer's concentrations in the pulled groundwater following incubation and C_0 was tracer's concentrations in the original pushed groundwater (Freeze and Cherry, 1979). The masses of dissolved N_2O-N and N_2-N gases (μg) were calculated from the headspace extraction samples using equations and constants provided by Mosier and Klemedtsson (1994). The total mass of N_2O-N or N_2-N was then transformed to the mass of $^{15}N_2O$-N or $^{15}N_2$-N multiplying it by the respective ^{15}N sample enrichment proportion (ratio of pulled atom% of the dissolved N_2O-N and N_2-N to pushed NO_3^--N atom%, both corrected for ambient atom%). Gas production rates for $^{15}N_2O$-N and $^{15}N_2$-N were expressed as μg N kg^{-1} soil d^{-1} following Eq. (1) below: