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Occurrence of the agricultural nitrification inhibitor, dicyandiamide, in surface waters and its effects on nitrogen dynamics in an experimental aquatic system

Ian Smith, Marc Schallenberg*

Department of Zoology, University of Otago, P.O. Box 56, Dunedin 9054, New Zealand

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ABSTRACT

Nitrification inhibitors are promoted to mitigate nitrate leaching and N_2O emissions from grazed pastures. We hypothesized that the nitrification inhibitor, dicyandiamide (DCD), appears in surface waters in agricultural areas where it is used and that DCD perturbs nitrogen cycling in surface waters as it does in soils. We sampled 15 streams and drains in a coastal lowland agricultural catchment and found measurable concentrations of DCD in many of the surface waters, with a maximum measured concentration of approximately 1000 $\mu g\,L^{-1}$. DCD concentrations were positively correlated with ammonium concentrations, the ratio of ammonium:nitrate, and electrical conductivity (salinity), while DCD concentrations were negatively correlated with dissolved oxygen concentrations. These results are consistent with DCD entering waterways via shallow groundwater seepage and having an inhibitory effect on in situ nitrification in the aquatic ecosystems.

A laboratory experiment using sediment–water mesocosms was conducted using sediment and water collected from a wetland located downstream of the surveyed streams and drains. Initially, high nitrate and low ammonium concentrations prevented nitrification in the mesocosms and the addition of DCD under these conditions stimulated apparent denitirification while having no effect on ammonium concentrations. After subsequent manipulations of the ammonium:nitrate ratio in the mesocosms, nitrification was stimulated and concentrations >600 $\mu g\,L^{-1}$ DCD inhibited nitrification, resulting in elevated concentrations of ammonium and reductions in nitrate concentrations compared to the control mesocosms (without DCD added). Although no change in dissolved inorganic nitrogen concentrations were observed in relation to DCD additions, these results indicate that DCD is effective at blocking in situ nitrification in aquatic systems and its presence may result in elevated ammonium concentrations and reduced nitrate concentrations. Such perturbations to N-cycling in aquatic ecosystems may have implications for ammonia toxicity, eutrophication and algal community composition. DCD loss rates measured in our mesocosms were more rapid than those previously reported for soils.

1. Introduction

Nitrogen is essential for plant growth and health and is often the growth limiting factor in agricultural systems. Intensive N fertilizer application has become the norm for dairy farms in New Zealand due to its importance to plant productivity and farm profitability (Parliamentary Commissioner for the Environment, 2006). However, the application of N fertilizers can often lead to the leaching of plant-available nitrate (NO_3^-) into surface waters (Beeton et al., 2008) and groundwater (Gibert et al., 2008) and the inputs of synthetic N fertilizers and stock wastes are the main causes of NO_3^- contamination of aquifers and surface waters throughout the world (Hallberg, 1989; Guimera, 1998), contributing to the eutrophication of many surface waters (Brodrick et al., 1988).

The use of nitrification inhibitors, including dicyandiamide (DCD), has been proposed as a means of reducing the leaching of agriculturally derived NO_3^- into waters and agricultural nitrification inhibitors are now commonly used in many countries including New Zealand, Australia (Chen et al., 2010) and the USA (Franzen, 2011). Nitrification inhibitors delay the oxidation of NH_4^+ to NO_2^- (without affecting the subsequent oxidation of nitrite to nitrate) by reducing the activity of the edaphic nitrifying bacteria, *Nitrosomonas* (Irigoyen et al., 2003; Sahrawat, 2004). Studies have shown that DCD can be effective in reducing nitrate leaching from mineralized organic matter and urine deposited onto grazed pastures (Francis et al., 1995; Di and Cameron, 2002, 2004; de Klein and Monaghan, 2011), with its efficacy being dependent on soil DCD concentration, temperature, moisture, pH, and organic matter content (Puttanna et al., 1999). While these studies demonstrate the

* Corresponding author. Tel.: +64 3 479 8403.
E-mail address: marc.schallenberg@otago.ac.nz (M. Schallenberg).

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efficacy of DCD in certain grazed pasture environments, we found no published studies on the effects of DCD on nitrogen cycling in temperate aquatic environments receiving runoff from land treated with DCD. While some studies have examined effects of nitrification inhibitors on greenhouse gas emissions from rice paddies (e.g. Xu et al., 2002), these have not specifically examined the effects of DCD on N solute concentrations in the floodwaters. Furthermore, rice paddies are agricultural production systems and findings from such systems have little relevance to natural temperate surface waters such as rivers and wetlands, which are the focus of this study.

When applied as recommended, DCD commonly reaches concentrations of 1000–3000 $\mu g\,L^{-1}$ in lysimeter leachate (Shepherd et al., 2012 and studies therein), suggesting that DCD could leach from soils into drainage waters and downstream aquatic ecosystems. Pelagic and benthic habitats can be important sites of nitrification in freshwaters (Vincent and Downes, 1981; Coci et al., 2010). The presence of DCD in the aquatic environment could potentially alter the absolute and relative concentrations of NH_4^+ and NO_3^- by shutting down nitrifying bacteria in these habitats resulting in a reduction in nitrate concentrations while producing a buildup of regenerated ammonium or ammonia. The latter effect could result in ammonia toxicity because, under alkaline conditions, ammoniacal-N ($NH_4^+ + NH_3$) is represented by its un-ionized form, ammonia (NH_3), which is toxic to native fish at concentrations between 750 and 2350 $\mu g\,NH_3\text{-}N\,L^{-1}$ and to salmonids at concentrations between 80 and 1090 $\mu g\,NH_3\text{-}N\,L^{-1}$ (USEPA, 1985; Richardson, 1997). Australia and New Zealand Guidelines for Fresh and Marine Water Quality (ANZECC, 2000) provide a pollution trigger level for ammoniacal-N for slightly disturbed lowland rivers of 21 $\mu g\,L^{-1}$ and indicate that levels below 900 $\mu g\,L^{-1}$ will safeguard 95% of aquatic species.

The presence of ammonium often inhibits nitrate uptake in phytoplankton and periphyton and many studies indicate that, in general, the algae take up ammonium preferentially to nitrate (e.g. Berman et al., 1984; Reuter and Axler, 1992; Axler and Reuter, 1996). Therefore, changes in the relative availability of NO_3^- vs. NH_4^+ caused by the presence of DCD in freshwater systems may alter phytoplankton and periphyton productivity in these systems. Furthermore, in systems where coupled nitrification/denitrification results in substantial fluxes of N_2 to the atmosphere, the presence of DCD could interrupt the conversion of ammonium to N_2 gas via nitrification/denitrification, resulting in a buildup of regenerated ammonium. As phytoplankton and periphyton communities are commonly N-limited in lakes (Schallenberg, 2004; Lewis and Wurtsbaugh, 2008) and rivers (Francoeur et al., 1999; Biggs and Kilroy, 2004), the disruption of denitrification and the accumulation of regenerated ammonium could stimulate algal growth and eutrophication.

Thus, there are numerous potential impacts of the widespread use of nitrification inhibitors on downsteam aquatic ecosystems. This study examines the potential effect of DCD on nitrogen cycling in surface waters of an agricultural catchment in New Zealand and in laboratory mesocosms containing sediment and water obtained from a wetland (Fig. 1). We hypothesize that DCD will occur in surface waters in an agricultural catchment and that its presence will influence dissolved nitrogen speciation in the waters by increasing in the ratio of $NH_4^+:NO_3^-$ via its inhibition of the microbial nitrification of regenerated ammonium.

We manipulated nitrate and ammonium concentrations in mesocosms containing natural wetland sediments and water to first facilitate denitrification and then nitrification. As it does in soils, we hypothesize that the presence of DCD in the water column would inhibit nitrification in aquatic mesocosms. As a result of nitrification inhibition, we hypothesized that water column concentrations of NO_3^- would decrease while concentrations of NH_4^+ and the ratio of $NH_4^+:NO_3^-$ would increase. Our experiment allowed us to test whether these perturbations to natural N cycling in an aquatic system could also lead to net changes in dissolved inorganic nitrogen (DI-N) concentrations.

2. Materials and methods

2.1. DCD analysis

A colorimetric method developed by Vilsmeier (1979) was used to measure DCD concentrations using a Shimadzu UVmini-1240 spectrophotometer with a 100 mm cuvette and standards of 20, 50, 200, 500, 1000 and 2000 $\mu g\,DCD\,L^{-1}$. The reaction of DCD with specified reagents forms a red complex at high pH, with a light absorbance peak at 535–540 nm. A linear calibration coefficient was determined ($R^2 = 0.998$). The detection limit (defined as 2 × standard deviation of 10 blanks of distilled, de-ionized water) was 25 $\mu g\,DCD\,L^{-1}$.

2.2. Taieri Plain survey

The Lower Taieri Plain is located ca. 20 km west-southwest of Dunedin, South Island, New Zealand (Fig. 2) and is situated near sea level. The Taieri River passes through the plain from north-east to south-west, which is also the general direction of groundwater flow (Kensington et al., 2004). The Taieri aquifer is composed of gravel and sand layers with a sand-silt aquiclude covering approximately two-thirds of the basin (Barrell et al., 1999). Soils are of alluvial origin. Gleyed soils (peat and silt loams), indicative of a raised water table, dominate the southwestern part of the plain, which is drained by the West Taieri Drainage Scheme. The northeastern part of the plain, in the immediate vicinity, and northeast of, the Taieri River, is comprised mainly of recent, less gleyed soils (silt loams), reflecting better water drainage (Leamy and Leslie, 1986). Agriculture is the dominant land use in the Taieri Plain, with dairying being most common on the western part of the plain.

Fifteen sampling sites were selected throughout the Taieri Plain, upstream of the Waipori/Waihola Lake-Wetland Complex (Fig. 2). The sampling area comprised a number of streams as well as drains constructed in former wetland areas (Table 1). Sites 1–12 were located within the West Taieri Drainage system and were fed wholly or partly by shallow groundwater seepage, with sites 1–8 exhibiting minor tidal water level variations. Sites 2, 13, 14 and 15 received stream flows fed by springs and non-agricultural surface runoff.

Surveys were conducted on 20 October and 11 November 2008, following the typical winter/early spring DCD application period. An additional survey was conducted on 21 January 2009, during mid-summer, but only 11 sites could be sampled in January because water levels and flows were too low to sample 4 of the sites. Each sample was collected in a 500 mL acid-washed glass bottle and was placed on ice while temperature, salinity, dissolved oxygen and conductivity data were recorded on site with a Yellow Springs Instrument Pro Plus meter. Once returned to the lab, approximately 40 mL of each sample was filtered through an acid-washed glass–fiber filter (0.7 μm nominal pore size) into an acid-washed 50 mL polyethylene tube which was then frozen at −20 °C.

Frozen samples were thawed for 12–18 h prior to analyses for dissolved nutrients and DCD. Once thawed, tubes were agitated and 2 mL was removed from each sample and set aside for colorimetric DCD analysis, as described above. The remaining portion of each sample was then analyzed for nitrate + nitrite-N (NN-N) and ammoniacal-N (measured as ammonium-N) concentrations using a Skalar SAN^{plus} System colorimetric auto-analyzer using standard