Groundwater nitrate reduction versus dissolved gas production: A tale of two catchments

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HIGHLIGHTS

- NO_3^- removal capacity was highly variable between and within study catchments.
- Hydrogeological and agronomic factors controlled groundwater hydrogeochemical signatures.
- NO_3^- consumption was coupled with excess N_2 and N_2O production.
- Excess N_2 was the dominant denitrification reaction product in near stream groundwater.
- Groundwater N_2O was a net source of greenhouse gas emissions in both catchments.

GRAPHICAL ABSTRACT
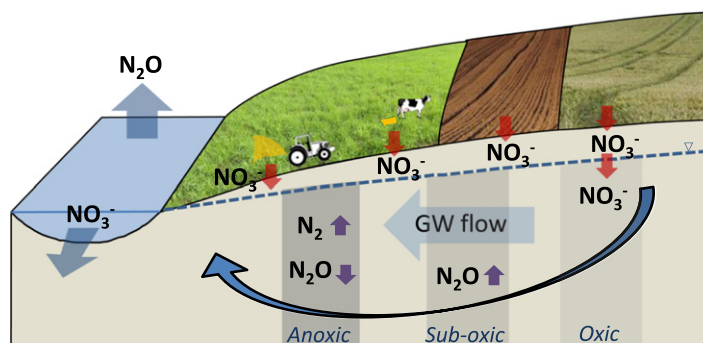
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ABSTRACT

At the catchment scale, a complex mosaic of environmental, hydrogeological and physicochemical characteristics combine to regulate the distribution of groundwater and stream nitrate (NO_3^-). The efficiency of NO_3^- removal (via denitrification) versus the ratio of accumulated reaction products, dinitrogen (excess N_2) & nitrous oxide (N_2O), remains poorly understood. Groundwater was investigated in two well drained agricultural catchments (10 km^2) in Ireland with contrasting subsurface lithologies (sandstone vs. slate) and landuse. Denitrification capacity was assessed by measuring concentration and distribution patterns of nitrogen (N) species, aquifer hydrogeochemistry, stable isotope signatures and aquifer hydraulic properties. A hierarchy of scale whereby physical factors including agronomy, water table elevation and permeability determined the hydrogeochemical signature of the aquifers was observed. This hydrogeochemical signature acted as the dominant control on denitrification reaction progress. High permeability, aerobic conditions and a lack of bacterial energy sources in the slate catchment resulted in low denitrification reaction progress (0–32%), high NO_3^- and comparatively low N_2O emission factors ($EF_{5g}1$). In the sandstone catchment denitrification progress ranged from 4 to 94% and was highly dependent on permeability, water table elevation, dissolved oxygen concentration solid phase bacterial energy sources. Denitrification of NO_3 — to N_2 occurred in anaerobic conditions, while at intermediate dissolved oxygen; N_2O was the dominant reaction product. $EF_{5g}1$ (mean: 0.0018) in the denitrifying sandstone catchment was 32% less than the IPCC default. The denitrification observations across catchments were supported by stable isotope signatures. Stream NO_3^- occurrence was 32% lower in the sandstone catchment even though N loading was substantially higher than the slate catchment.

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1. Introduction

Anthropogenic application of inorganic and organic nitrogen (N) fertilisers to agricultural landscapes has pervasive consequences including human health implications (e.g. methemoglobinaemia), eutrophication, aquatic acidification, loss of habitat biodiversity and greenhouse gas emissions (Dennis et al., 2012; Gruber and Galloway, 2008; Richards et al., 2015; Weymann et al., 2008). In light of agricultural intensification, the identification of subsurface environments with a natural capacity to attenuate excess N is essential to the development of sustainable management strategies. Globally, denitrification is regarded as the dominant nitrate (NO_3^-) attenuation mechanism in groundwater (Korom, 1992; Rivett et al., 2008; Seitzinger et al., 2006). Denitrification is a microbially mediated process whereby NO_3^- is reduced to dinitrogen (N_2) gas. In baseflow dominated catchments, groundwater denitrification has the capacity to mitigate stream water N enrichment by returning N to the long residence time atmospheric pool (Heffernan et al., 2012). Denitrification can represent an environmentally positive nitrate removal process (Schipper and Vojvodić-Vuković, 2001); however such a characterisation is subject to an important caveat. The reaction is sequential and as such there are several intermediary products including nitrite (NO_2^-), nitric oxide (NO) and nitrous oxide (N_2O). The differentiation between which reaction product is dominant is of key environmental concern: N_2 gas is environmentally benign whereas N_2O is a potent greenhouse gas, while NO contributes to stratospheric ozone depletion, eutrophication and formation and accumulation of surface ozone (Vitousek et al., 1997).

In groundwater, a number of geochemical criteria must be met for denitrification to occur. Studies documenting the relationship between NO_3^- concentrations and aquifer physicochemistry are prevalent in the available literature (Brettar et al., 2002; Jahangir et al., 2012a; Rissmann, 2011). A commonality throughout indicates that the presence of denitrifying bacteria, reducing conditions and the availability of bacterial energy sources create zones of enhanced denitrification potential. Traditionally, it has been believed that that groundwater denitrification is predominantly heterotrophic with rates related to the amount of dissolved organic carbon (DOC) coupled with the wide abundance of denitrifiers in the groundwater (Barrett et al., 2013; Rivett et al., 2008). Recent research however suggests that autotrophic denitrification i.e. oxidation of solid phases within an aquifer such as Iron (Fe) and Manganese (Mn) may in fact drive bacterial NO_3^- reduction (Green et al., 2008; Heffernan et al., 2012). Great uncertainty surrounds the spatial and temporal distribution of denitrifying zones, owing to a confounding hierarchy of scale. In essence, an aquifer can be visualised as an environmental ecosystem, which is capable of removing between 0 and 100% of reactive N. The geological history of the aquifer (mineralogy, stratigraphy and weathering) at the catchment scale controls the distribution and availability of bacterial energy sources, aquifer flow paths, permeability and connectivity at the sub metre scale (Seitzinger et al., 2006). These physical factors in turn determine the hydrogeochemical signature and N attenuating capacity of the aquifer, while agronomy, soil type, hillslope geometry and meteorology control the temporal N load passing through the ecosystem. In complex geological environments, an entire aquifer or catchment cannot be characterised as having high or low denitrification potential. Denitrification is enhanced in certain spatial zones or hot spots (Jahangir et al., 2012a, 2013) and it is the location and intensity of these hot spots in relation to a receptor e.g. a stream, which is paramount to characterising the potential for natural attenuation of N in an aquifer. Several studies have measured denitrification based upon NO_3^- loss (Jahangir et al., 2012a; Thayalakumaran et al., 2008; Tsushima et al., 2002), however NO_3^- gradients can result from temporal patterns of source contribution (Seitzinger et al., 2006) and other NO_3^- removal pathways such as plant and microbial assimilation, dissimilatory NO_3^- reduction to ammonium (NH_4^+) and anaerobic oxidation of NH_4^+ (Jahangir et al.,

2016). Studies based solely on NO_3^- dynamics have a capacity to overestimate the contribution of denitrification on NO_3^- removal rates (Green et al., 2008). Directly measured denitrification rates based upon the natural accumulation of denitrification products (N_2O & N_2) in groundwater are rare with calculated values spanning orders of magnitude across studies (Green et al., 2008; Heffernan et al., 2012; Jahangir et al., 2013; Weymann et al., 2008). $^{15}N_{NO3}$ isotopic signatures have been used extensively to calculate N sources and processes (Kendall et al., 2007). A dual isotopic approach ($^{15}N_{NO3}$ and $^{18}O_{NO3}$) can be used to infer both the source of NO_3^- to groundwater and also transformational processes such as denitrification (Wassenaar, 1995). Although it is not possible to directly calculate denitrification rates from isotopic signatures, coupled enrichment of $^{15}N_{NO3}$ and $^{18}O_{NO3}$ provides a powerful tool to identify areas of enhanced denitrification (Baily et al., 2011).

Contemporaneous measurements of both N_2O and N_2 in groundwater not only provide evidence of NO_3^- removal pathways but also offer an insight into the concept of pollutant swapping of NO_3^- for N_2O. Globally it is estimated that agricultural practises are responsible for in excess of 60% of anthropogenic N_2O emissions (Harty et al., 2016). The International Panel on Climate Change (IPCC) subdivides agricultural N_2O into three categories: direct emissions from agricultural land, emissions from animal management strategies and indirect emissions of N_2O that is either volatilised, leached or removed in biomass (IPCC, 1997). Each subcategory is estimated to contribute one third of the total agricultural N_2O source with indirect emission estimations contributing two thirds of the uncertainty (Penman, 2000). There exists a substantial body of research into the contribution N_2O to the global greenhouse gas budget via direct pathways i.e. from soil to the atmosphere (Bouwman, 1990; de Klein et al., 2001; Li et al., 2011, 2013; Soussana et al., 2007). Large uncertainties remain around the contribution of indirect N_2O emission pathways, namely from groundwater and surface drainage, rivers and coastal marine areas (Vilain et al., 2012). Fuelling this uncertainty is a lack of process based understanding regarding the production, consumption and movement of groundwater and stream N_2O across a range of hydrogeological settings (Clough et al., 2007; Höll et al., 2005; Jahangir et al., 2013). In 1997, the IPCC published an emission factor of 0.015 for the fraction of agriculturally derived N_2O released from groundwater sources (Mosier et al., 1999). In 2006, the IPCC default value was amended to 0.0025 (de Klein et al., 2006) based upon the combined reviews of Hiscock et al. (2003), Reay et al. (2005) and Sawamoto et al. (2005). While this downward revision indicated that groundwater derived N_2O was less significant than previously proposed, the published range of uncertainty (0.0005–0.025) highlighted the ambiguity surrounding the natural variability of N_2O in groundwater while reinforcing the need for further research to constrain emission factors and reduce uncertainty. Studies combining a complete analysis of N species: organic N, ammonium (NH_4^+–N), NO_3^-–N, nitrite (NO_2^-–N), N_2O–N & N_2–N, with aerobicity (dissolved oxygen and redox potential), electron donors, dual isotopic techniques and aquifer hydraulic properties are rare. It is only through the refinement of scale, from catchment to sub metre, that a process based understanding of groundwater N removal can be developed.

The objectives of this study are (1) to quantify the capacity of hillslope hydrologic systems to naturally attenuate agriculturally derived NO_3^-, 2) to elucidate the extent of denitrification by measuring the accumulation and ratio of reaction products (N_2 and N_2O) and (3) to identify the physical and biogeochemical factors affecting groundwater denitrification rates and indirect N_2O emissions from groundwater.

2. Materials & methods

2.1. Study sites

This research was undertaken along four hillslopes of varying length, geometry and landuse in two agricultural catchments in the Republic of