



Nitrous oxide as an indicator of nitrogen transformation in a septic system plume



L. Li^a, J. Spoelstra^{a,b,*}, W.D. Robertson^a, S.L. Schiff^a, R.J. Elgood^a

^aUniversity of Waterloo, Waterloo, ON N2L 3G1, Canada

^bEnvironment Canada, Burlington, ON L7R 4A6, Canada

ARTICLE INFO

Article history:

Received 30 April 2014

Received in revised form 26 August 2014

Accepted 15 September 2014

Available online 28 September 2014

This manuscript was handled by Laurent Charlet, Editor-in-Chief, with the assistance of Rafael Pérez-López, Associate Editor

Keywords:

Nitrous oxide
Septic system
Stable isotopes
Nitrification
Denitrification
Ground water

SUMMARY

This study evaluates the use of ground water N₂O concentration and stable isotope composition for providing insights into nitrogen cycling processes in a large septic system plume in southern Ontario, Canada. An extremely large range of dissolved N₂O concentrations were measured (0.4–1071 µg N/L) that were higher than atmospheric equilibrium values of ~0.3 µg N/L, demonstrating substantial N₂O production in the subsurface. The highest N₂O concentrations occurred around the periphery of a mid-depth zone where NO₃⁻ attenuation, elevated DOC concentration, and NO₃⁻ stable isotope ratios provided evidence that denitrification was occurring. Broad ranges in δ¹⁵N–N₂O (–45.8‰ to +30.6‰) and δ¹⁸O–N₂O (+20.4‰ to +96.0‰) were evident. Using literature isotopic enrichment factors, which differ for N₂O produced during nitrification and denitrification, and measured ranges of plume NH₄⁺ and NO₃⁻ isotopic ratios, zones of both nitrifier-derived N₂O (shallow zone) and denitrifier-N₂O (mid-depth and deeper zones) could be identified. Time series sampling showed that nitrifier N₂O was present early in the summer season (June) but then denitrifier N₂O was more dominant later in the season. In a mid-depth NO₃⁻ depleted zone, the production of denitrifier-N₂O was evident early in the season when ¹⁵N and ¹⁸O enrichment of NO₃⁻ was not sufficiently advanced to be indicative of denitrification, although δ¹⁵N and δ¹⁸O values of NO₃⁻ increased later in the season. The analysis of N₂O concentrations and stable isotopic composition, in conjunction with conventional chemical analyses, provides insights into N-cycling processes in the Long Point ground water septic plume. However, large ranges in the isotopic composition of N₂O produced by nitrifiers and denitrifiers meant that δ¹⁵N and δ¹⁸O analysis of ground water N₂O provided qualitative, rather than quantitative, information on denitrifier versus nitrifier production of N₂O at this site.

Crown Copyright © 2014 Published by Elsevier B.V. All rights reserved.

1. Introduction

Denitrification, whereby nitrate (NO₃⁻) is sequentially reduced to nitrite (NO₂⁻), nitric oxide (NO), nitrous oxide (N₂O), and finally to nitrogen gas (N₂), is recognized as the dominant NO₃⁻ attenuation process in ground water (Rivett et al., 2008). However, denitrification does not always occur and the process can be difficult to detect and quantify (Groffman et al., 2006). Consequently, a variety of approaches have been developed to identify and measure denitrification activity. These include tracer methods, N₂ quantification, molecular biochemical methods and mass balance approaches (Groffman et al., 2006). One approach to assessing denitrification

activity in ground water is through the analysis of NO₃⁻ stable isotope ratios (δ¹⁵N and δ¹⁸O) (e.g. Amberger and Schmidt, 1987; Mariotti et al., 1988; Böttcher et al., 1990; Aravena and Robertson, 1998; Mengis et al., 1999). During denitrification, enrichment of both ¹⁵N and ¹⁸O occurs in the residual NO₃⁻ (Böttcher et al., 1990; Granger et al., 2004, 2008). In ground water studies, denitrification N isotope enrichment factors (ε¹⁵N_{(N₂-NO₃⁻)) in the range of –13.9‰ to –30‰ have been reported and δ¹⁸O and δ¹⁵N values of the residual NO₃⁻ increase at a ratio of approximately 1:2 as NO₃⁻ is consumed (Vogel et al., 1981; Böttcher et al., 1990; Aravena and Robertson, 1998; Mengis et al., 1999; Chen and MacQuarrie, 2005; Granger et al., 2008).}

This study examines the usefulness of dissolved N₂O concentration and isotope ratios for providing insights into nitrogen (N) cycling processes occurring in ground water, particularly as an indicator of denitrification activity in a septic plume. N₂O is a greenhouse gas that has a global warming potential approximately

* Corresponding author at: National Water Research Institute, Environment Canada, Canada Centre for Inland Waters, 867 Lakeshore Road, P.O. Box 5050, Burlington, ON L7R 4A6, Canada. Tel.: +1 (905) 336 6246; fax: +1 (905) 336 6430.
E-mail address: John.Spoelstra@ec.gc.ca (J. Spoelstra).

300 times that of carbon dioxide (IPCC, 2007) and the atmospheric concentration (~ 320 ppb) is currently increasing at a rate of 0.25% per year (Denman et al., 2007) as a result of anthropogenic activities (Olivier et al., 1998; Mosier et al., 1998; Kroeze et al., 1999; Stein and Yung, 2003; Snider et al., in preparation). Although measuring NO_3^- isotope ratios is a widely used approach to detect denitrification activity, the isotopic composition of NO_3^- in most ground waters exhibit considerable variability and therefore substantial NO_3^- loss is normally required before ^{15}N and ^{18}O isotopic enrichment of the residual NO_3^- is sufficiently pronounced to be definitive with respect to denitrification. In contrast, dissolved N_2O analysis by headspace gas chromatography has a detection limit (~ 0.1 $\mu\text{g N/L}$ or lower) that is several orders of magnitude more sensitive than that for NO_3^- concentrations. Thus, soon after denitrification starts in ground water, excess N_2O may be detected and thereby provides an early indication of the onset of this important attenuation process, much earlier than with the use of conventional NO_3^- isotope methods. In addition, the analysis of N_2O is easier than measuring N_2 excess, which is complicated by the high atmospheric N_2 concentration that can easily contaminate samples during handling and analysis.

In subsurface environments, N_2O is mainly produced as an intermediate product of nitrifier denitrification and dissimilatory denitrification (Garcia-Ruiz et al., 1998; Russow et al., 2000), collectively referred to as denitrification hereforth. N_2O can also be produced as an alternate product of the oxidation of hydroxylamine during nitrification of ammonium (NH_4^+) to NO_2^- and NO_3^- . N_2O production via hydroxylamine oxidation has been demonstrated to occur in laboratory cultures (Otte et al., 1999; Sutka et al., 2003, 2004, 2006) but its importance in natural systems is not known.

The ratio of $\text{N}_2\text{O}:\text{N}_2$ production during dissimilatory denitrification can vary with temperature, NO_3^- concentration, availability of electron donors (e.g. dissolved organic carbon (DOC)), and oxygen gas (O_2) concentration (Bouwman, 1990). The microbial community active in ground water also affects the ratio of N_2O produced as some microorganisms lack the N_2O reductase enzyme and therefore cannot further reduce N_2O to N_2 (Philippot et al., 2011). Once produced, N_2O can persist in ground water and may be subsequently released to the atmosphere when ground water discharges to surface, or it may be further reduced to N_2 .

A couple of studies have previously investigated the usefulness of N_2O stable isotope ratios for distinguishing N_2O production and cycling processes in ground water. Studies of ground water beneath a forested watershed in Japan (Koba et al., 2009) and aquifers underlying agricultural land in Northern Germany (Well et al., 2012) both concluded that, even with isotopomer analysis used, accurate quantitative information on the fraction of ground water N_2O produced by nitrification versus denitrification could not be elicited, nor could quantitative information on the degree of subsequent N_2O reduction. Reasons for the lack of quantifiability include, (1) the large range of isotope effects for N_2O production via the different pathways, (2) uncertainty in the isotopic composition of the NH_4^+ and NO_3^- sources, (3) uncertainty with respect to the degree of oxygen (O) exchange occurring during nitrification and denitrification, and (4) spatial and temporal heterogeneity with respect to the above factors. However, the stable isotope techniques can still provide qualitative information on the relative importance of N_2O production pathways. For example, in the Koba et al. (2009) study, both $\delta^{18}\text{O}-\text{N}_2\text{O}$ versus $\delta^{15}\text{N}^{\text{bulk}}-\text{N}_2\text{O}$ and isotopomer analysis indicated that denitrification was the dominant N_2O production reaction.

The goal of this study was to evaluate the usefulness of N_2O as a sensitive tool for indicating nitrification and denitrification activity in a well-studied ground water septic plume. Our research approach was to examine the production of N_2O within a NO_3^-

and NH_4^+ rich ground water environment (Long Point septic system plume) where nitrification and denitrification were known to be occurring in the unsaturated and saturated zones, respectively (Aravena and Robertson, 1998; Robertson et al., 2012). We are not aware of previous studies that have examined the stable isotope composition of N_2O in a septic system plume.

2. Methods

2.1. Long Point site

The Long Point campground, located on the north shore of Lake Erie, Ontario, Canada (Fig. 1), has 256 overnight campsites and is open seasonally from mid-May until mid-October. Sewage from a single washroom facility is pump-dosed to two tile beds (~ 290 m^2 each). Loading to the tile beds during peak use from June 28 to September 6, 2010 is estimated at ~ 7 cm/day based on metered water usage, a value similar to previous estimates (~ 10 cm/day ; Robertson and Cherry, 1995). Tile bed 2, which is the focus of the current study, has been subject to detailed ground water monitoring since its commissioning in 1990. The plume from tile bed 2 flows southward toward L. Erie within a ~ 5 m thick unconfined calcareous sand aquifer. The plume is easily distinguished from the pristine background ground water at the site by a prominent core zone that has elevated Cl^- of 40–70 mg/L , similar to the septic tank effluent value and exhibiting little dilutive mixing with background ground water (Fig. 2). Ground water temperatures in the plume core range from 11 to 14 $^\circ\text{C}$. Plume ages vary from about seven days in the shallow water table zone below the tile bed to about one year at the most distal piezometer nests used in this study, located 17 m from the edge of the tile bed (Robertson et al., 2012). The horizontal ground water velocity, averaged over the entire season was estimated previously at 23 m/yr , although higher horizontal flows of about 40 m/yr occur during heavy sewage loading in the summer (Robertson, 2008). The presence of a 2 m thick sandy vadose zone below the tile bed normally provides relatively complete oxidation of the wastewater and results in high NO_3^- -N concentrations of up to ~ 100 mg/L in the shallow plume zone below the tile bed. The plume is suboxic however (dissolved oxygen < 1 mg/L , Aravena and Robertson, 1998; Robertson et al., 2012) and at depth, NO_3^- is attenuated by denitrification promoted by trace quantities of organic carbon and biogenic pyrite contained in the aquifer sediments (Aravena and Robertson, 1998).

2.2. Field methods

Site characterization and ground water sampling procedures have been described previously (e.g. Aravena and Robertson, 1998). In the current study, ground water samples for dissolved N_2O concentrations and isotope analyses were collected on six occasions during 2008–2009 (full transect, June 17, 2008 and September 11, 2008; tile bed nest LP 100, June 2, June 24, July 24 and October 13, 2009). Sampling on June 24, 2009 also included collection of vadose zone pore gas samples at nest LP 100 (Fig. 2). Seven pore gas samples were collected from 0.3 to 1.0 m depth using a steel tube advanced into the subsurface and following collection procedures described by Spoelstra et al. (2007).

Ground water samples for N_2O concentration and isotope analysis were collected in 60 mL and 160 mL serum bottles, respectively. Bottles were filled with unfiltered ground water to overflowing, and then a rubber stopper (BD Vacutainer[®]) with a hypodermic needle was inserted into the bottle resulting in a headspace-free sample. Needles were then removed and the

Download English Version:

<https://daneshyari.com/en/article/6412021>

Download Persian Version:

<https://daneshyari.com/article/6412021>

[Daneshyari.com](https://daneshyari.com)