



Nitrate distribution and potential attenuation mechanisms of a municipal water supply bedrock aquifer



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ABSTRACT

The Silurian bedrock aquifer constitutes a major aquifer system for groundwater supply across the Ontario province in Canada. The application of natural and industrial fertilizers near urban centers has led to groundwater NO_3^- -N concentrations that sometimes have exceeded the drinking water limit, posing a threat to the usage of groundwater for the human consumption. Therefore, there is a growing interest and concern about how nitrate is being leached, transported and potentially attenuated in bedrock aquifers. This study assesses the local distribution of groundwater NO_3^- in the up-gradient area of two historically impacted municipal wells, called Carter Wells, in the City of Guelph, Canada, in order to evaluate the potential nitrate attenuation mechanisms, using both groundwater geochemical and isotopic analysis (^3H , $\delta^{15}\text{N}$ - NO_3 , $\delta^{18}\text{O}$ - NO_3 , $\delta^{18}\text{O}$ - SO_4 , $\delta^{34}\text{S}$ - SO_4) and a detailed vertical hydrogeological and geochemical bedrock characterization. The results indicate that probably the main source of nitrate to the Carter Wells is the up-gradient Arkell Research Station (ARS), an agricultural research facility where manure has been historically applied. The overburden and bedrock groundwater with high NO_3^- concentrations at the ARS exhibits a manure-related $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ signature, isotopically similar to the high nitrate in the down-gradient groundwater from domestic wells and from the Carter Wells. The nitrate spatial distribution appears to be influenced and controlled by the geology, in which more permeable rock is found in the Guelph Formation which in turn is related to most of the high NO_3^- groundwater. The presence of an underlying low permeability Eramosa Formation favors the development of oxygen-depleted conditions, a key factor for the occurrence of denitrification. Groundwater with low NO_3^- -N concentrations associated with more oxygen-limited conditions and coincident with high SO_4^{2-} concentrations are related to more enriched $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ values in NO_3^- and to more depleted $\delta^{34}\text{S}$ and $\delta^{18}\text{O}$ values in SO_4^{2-} , suggesting that denitrification coupled with pyrite oxidation is taking place. The presence of macro-crystallized and disseminated pyrite especially in the Eramosa Formation, can support the occurrence of this attenuation process. Moreover, based on tritium analysis, some denitrification can occur in shallow bedrock and within relatively short residence times, associated with less permeable conditions in depth which facilitates oxygen consumption through sulfide oxidation. The role of denitrification mediated by organic carbon cannot be discarded at the study site. This study suggests that the geological configuration and particularly the presence of low permeability Eramosa Formation can play an important role on nitrate natural attenuation, which may serve as a decision factor on defining the bedrock water supply system for both domestic and municipal purposes.

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1. Introduction

Nitrate (NO_3^-) is one of the most ubiquitous contaminants in

groundwater (Spalding and Exner, 1993), potentially leading to health and environmental problems (WHO, 2007). Many urban centers obtain their water supply from groundwater, even when surface water availability is not an issue. Furthermore, groundwater sustains surface water baseflow and therefore surface water and groundwater are linked. As a long term water resource, groundwater can be less susceptible to contamination than surface water due to much longer travel times and reactive processes. However,

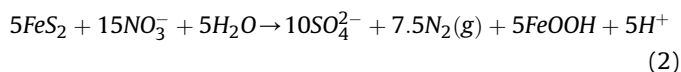
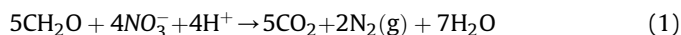
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increasing population and intensive agriculture have led to noticeable NO_3^- contamination impacts to groundwater quality worldwide. In particular, one of the key factors to groundwater nitrate contamination is the persistent application of natural and industrial fertilizers to soils often leading to NO_3^- -N concentrations that exceed the drinking water limit (DWL) of 10 mg/L (Spalding and Exner, 1993; Böhlke, 2002; Schröder et al., 2004; Wick et al., 2012).

In regions where fractured bedrock aquifers provide water supply, there is a growing interest and concern about how nitrate is being leached, transported and potentially attenuated (Pauwels et al., 2000; Tarits et al., 2006; Einsiedl and Mayer, 2006; among others). In fractured media, fracture flow can play a key role in mass transport processes as fractures can represent preferential pathways for rapid contaminant migration. On the other hand, solute flux and contaminant advance can be decreased or delayed by attenuation processes such as dispersion, matrix diffusion, or chemical reduction.

One of the most efficient ways of removing NO_3^- from groundwater is by denitrification (Korom, 1992; Gurdak and Qi, 2012), a biochemical process that converts nitrate into N_2 gas, mediated by bacteria, in the presence of electron donors under reducing conditions. Denitrification is well documented in porous aquifers in which both organic matter and inorganic compounds as electron donors play important roles (Postma et al., 1991; Aravena and Robertson, 1998; Mohamed et al., 2003; Schwientek et al., 2008; Stenger et al., 2008; Jørgensen et al., 2009; Zhang et al., 2009, 2012). Studies from fractured bedrock aquifers have revealed that denitrification can also occur in these environments (Mariotti et al., 1988; Pauwels et al., 2000; Tarits et al., 2006; Vitòria et al., 2008; Hiscock et al., 2011) and have shown that reduced sulfide minerals (e.g. pyrite) and ferrous iron (Fe^{2+}) can be primary electron donors for denitrification even under the presence of organic matter. These reactions (Korom, 1992; Appelo and Postma, 2005; Aravena and Mayer, 2010) can be summarized as follows:



Chemical and isotopic tracers can be used as evidence to document the occurrence of these reactions in groundwater. Isotopic analysis of NO_3^- has been proven to be a useful tool to identify denitrification, as isotopic fractionation during nitrate reduction in both reactions produces an enrichment of $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ values in the residual NO_3^- (Aravena and Robertson, 1998; Fukada et al., 2004; Aravena and Mayer, 2010). During denitrification mediated by organic carbon, which is characterized by $\delta^{13}\text{C}$ values between -25‰ and -29‰ (Wassenaar et al., 1991), a trend of increasing dissolved inorganic carbon concentration correlated with a trend toward more depleted $\delta^{13}\text{C}$ values in the DIC (Nascimento et al., 1997) can be used as evidence to document the occurrence of the first reaction in groundwater (Equation (1)). In case of the second reaction, increasing sulfate (SO_4^{2-}) concentrations in bedrock groundwater concomitant with NO_3^- reduction has been widely used as evidence of autotrophic denitrification mediated by pyrite and ferrous iron oxidation (Equation (2)), provided that there is no significant SO_4^{2-} contribution from other sources (Moncaster et al., 2000; Tarits et al., 2006; Levison and Novakowski, 2008; Otero et al., 2009; Pauwels et al., 2010).

As this reaction does not produce significant isotopic fractionation in sulfate (Seal, 2006; Aravena and Mayer, 2010), fingerprinting using $\delta^{34}\text{S}$ and $\delta^{18}\text{O}$ combined provides crucial information

regarding the origin of groundwater SO_4^{2-} . In particular, sulfide minerals often present a characteristic negative isotopic fingerprint that can be identified in the resultant SO_4^{2-} in solution (Aravena and Robertson, 1998; Aravena and Mayer, 2010; Farquhar et al., 2010).

The City of Guelph, Canada, relies almost exclusively on groundwater from a Silurian dolostone bedrock aquifer for its potable water supply. Although many municipal wells are located in urban and near agricultural areas, there is a limited number of groundwater quality assessments (Golder, 2006; AquaResource, 2010a), and there is no literature regarding NO_3^- contamination in the city bedrock aquifer. In particular, the processes and key factors governing groundwater NO_3^- distribution in this bedrock aquifer are not completely understood. Groundwater from two neighboring municipal wells near the city, called Carter Wells, has presented nitrate concentrations persistently near and above the DWL since 2001 decreasing only after 2010 (AquaResource, 2010b). In order to effectively improve policy and management practices to protect bedrock groundwater as a safe drinking-water resource, understanding the processes affecting nitrate fate and transport is crucial. The purpose of this study was to assess the local distribution of groundwater NO_3^- in the Silurian dolostone bedrock aquifer in the upgradient area of the Carter Wells, and to evaluate the potential nitrate attenuation processes by the combined use of geochemical (redox parameters, major and minor ions) and isotopic (^3H , $\delta^{15}\text{N}$ - NO_3 , $\delta^{18}\text{O}$ - NO_3 , $\delta^{18}\text{O}$ - SO_4 , $\delta^{34}\text{S}$ - SO_4) analysis of groundwater. This study used a network of piezometer nests and domestic wells located in the up-gradient area of the Carter Wells. A detailed vertical hydrogeological and geochemical characterization of the bedrock units was also performed at two locations along the regional groundwater flow direction.

2. Study site

The study site is a 14 km² agricultural area located to the southeast of the City of Guelph, Canada (Fig. 1). Annual precipitation reaches 923 mm/yr whereas potential evapotranspiration is estimated as 666 mm/yr (Golder, 2006). Land use in the area is mainly concentrated towards agricultural activities, although a current expansion of the City of Guelph is transforming previous crop fields into urbanized areas. Scattered rural residential areas present self-water supply through domestic wells and household septic systems. Investigations regarding crop practices have been historically carried out at the Arkell Research Station (ARS), a university facility, where the use of manure as an organic fertilizer has been a common practice (Fig. 1). As a result, overburden and shallow bedrock groundwater has been locally impacted by nitrate contamination (Unc, 1999).

Three municipal wells are located in the study area: Scout Camp well, Carter Wells, and Burke well. The Carter Wells are composed of two very proximal wells that for practical purposes are treated as one well. These wells differentiate from the rest of the city wells as they draw water from the shallow Guelph Aquifer. This aquifer is not protected by an aquitard so Carter Wells are more susceptible to contamination than the other wells of the city. In fact, nitrate contamination has been identified as a threat for these wells as NO_3^- -N concentrations have reached value near or above the drinking water limit of 10 mg/L between 2001 and 2010 (Fig. S1 in Supporting Information). However, a trend of decreasing nitrate concentration to values lower than the DWL has been observed in this well during the last 3 years, which could be related to reduction on nitrate input in the up-gradient areas and changes in pumping regime of the Carter Wells. The main potential sources of nitrate in the up-gradient areas are the ARS site and septic systems associated with recent urban development.

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