Nitrogen speciation and trends, and prediction of denitrification extent, in shallow US groundwater ☆

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SUMMARY

Uncertainties surrounding nitrogen cycling complicate assessments of the environmental effects of nitrogen use and our understanding of the global carbon–nitrogen cycle. In this paper, we synthesize data from 877 ambient-monitoring wells across the US to frame broad patterns of nitrogen speciation and trends. At these sites, groundwater frequently contains substantial co-occurring NO_3^- and XSN_2 (N_2 from denitrification), reflecting active/ongoing denitrification and/or a mixture of undenitrified and denitrified groundwater. NO_3^- and NH_4^+ essentially do not co-occur, indicating that the dominant source of NH_4^+ at these sites likely is not dissimilatory reduction of NO_3^- to NH_4^+. Positive correlations of NH_4^+ with apparent age, CH_4, dissolved organic carbon, and indicators of reduced conditions are consistent with NH_4^+ mobilization from degradation of aquifer organic matter and contraindicate an anthropogenic source of NH_4^+ for most sites. Glacial aquifers and eastern sand and gravel aquifers generally have lower proportions of NO_3^- and greater proportions of XSN_2 than do fractured rock and karst aquifers and western sand and gravel aquifers. NO_3^- dominates in the youngest groundwater, but XSN_2 increases as residence time increases. Temporal patterns of nitrogen speciation and concentration reflect (1) changing NO_3^- loads over time, (2) groundwater residence-time controls on NH_4^+ mobilization from solid phases, and (3) groundwater residence-time controls on denitrification. A simple classification tree using readily available variables (a national coverage of soil water depth, generalized geology) or variables reasonably estimated in many aquifers (residence time) identifies categorical denitrification extent (<10%, 10–50%, and >50%) with 79% accuracy in an independent testing set, demonstrating a predictive application based on the interconnected effects of redox, geology, and residence time.

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1. Introduction

Groundwater nitrogen (N) is a concern from standpoints of human health (NO_3^-) and eutrophication in surface-water bodies receiving groundwater discharge (NO_3^-, NH_4^+). As an integral part of the carbon-nitrogen cycle, N is also increasingly being studied in its relation to climate change (Gruber and Galloway, 2008). Emphasizing the importance of the N cycle as a global issue, Rockström et al. (2009) suggest that perturbation of the N cycle may already have exceeded planetary limits that protect Earth's self-regulation of the environment. Complicating assessments of N source, transport, and fate are great uncertainties in N fate, especially at regional to global scales (Galloway et al., 2008). Thus, there is a need for improved characterization of the spatial and

temporal variations in N species distribution in different environmental compartments and better understanding of processes controlling these variations. Groundwater is one of these key environmental compartments where N loading, storage, transformation, and transport are spatially and temporally variable and poorly characterized, particularly at large spatial scales.

Regional and national assessments of selected N species in groundwater are not lacking in the literature. For example, national assessments have been done for NO_3^- (e.g., Korea: Lee et al., 2007; US: Burow et al., 2010; The Netherlands: Mendizabal et al., 2012), and sometimes both NO_3^- and NH_4^+ (e.g., Denmark: Jørgensen and Stockmarr, 2009; New Zealand: Daughney et al., 2012). However, comprehensive analyses of broader suites of N species in groundwater at large spatial scales are uncommon. Similarly, although much is known about N cycling at selected groundwater research sites, characterization of the dominant sources of individual N species or their transformations at aquifer and national scales has received less attention. For example, although denitrification is a critically important route of NO_3^- loss in groundwater (e.g., Seitzinger et al., 2006; Rivett et al., 2008), less clear is the degree of importance of dissimilatory reduction of NO_3^- to

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NH_4^+—a NO_3^- transformation process and NH_4^+ source that might be locally important (Tiedje et al., 1982; Korom, 1992), but that has not received much examination in the context of larger groundwater systems.

In this contribution, a new database of 877 analyses of the major N species (NO_3^-, N_2 derived from denitrification, and NH_4^+) is used to explore spatial and temporal patterns of N speciation in an assessment of groundwater from the shallower portions of selected principal aquifers (US Geological Survey, 2003) in the 48 contiguous states of the US. The widely distributed nature of the ambient-monitoring dataset allows identification of broad spatial patterns. Temporal patterns are elucidated through the use of apparent (piston-flow) ages derived from environmental tracer data. Although only a subset of the 877 sites have estimates of apparent ages, an additional, published dataset of selected N species and apparent ages collected from a set of "transect-well" sites from local-scale groundwater-transect-based studies (Puckett et al., 2011) is added to increase the number of age-dated sites, and this combined dataset is used for analysis of temporal aspects of N speciation. Relations between NO_3^- and apparent age, and NH_4^+ and apparent age, also are used along with other evidence to infer origin of those N species in groundwater. Finally, N species and ancillary data are used to develop an explanatory classification tree (based on measured redox indicator species) and a predictive classification tree (based on readily available variables) to demonstrate methods capable of explaining patterns in N speciation (monitored sites with redox data) and predicting such patterns (unmonitored sites).

2. Approach and methods

2.1. Groundwater databases

The primary dataset, 877 widely distributed US Geological Survey (USGS) National Water-Quality Assessment (NAWQA) Program (http://water.usgs.gov/nawqa/) ambient-monitoring wells, was assembled for this paper. The wide spatial coverage of these data provides the foundation for most of the analysis of spatial patterns of N speciation. Another NAWQA dataset, one from transect-well sites (Puckett et al., 2011), was brought into the analysis to increase the number of age-dated sites for refined temporal characterization.

2.1.1. Ambient-monitoring database

Groundwater samples were collected from 877 monitoring and supply wells that are part of ambient-monitoring networks (Gilliom et al., 1995). Supply wells were primarily domestic wells, although some other well types, such as public supply or irrigation wells, also were included. These monitoring and supply wells belong to well networks, including (1) NAWQA Land Use Studies—shallow wells (primarily monitoring wells) randomly distributed in recharge areas of various classes of agricultural and urban land use, and (2) NAWQA Major Aquifer Studies—randomly distributed wells (primarily supply wells) tapping the shallow, used resource. Some (<10%) reference and miscellaneous wells (primarily monitoring wells) also were included. The spatial distribution of these sites is shown in Fig. S1 in supporting information.

Groundwater samples were analyzed for major dissolved gases [N_2, Ar, CH_4, CO_2, and (laboratory) O_2], environmental (age-dating) tracers (chlorofluorocarbons, SF_6, and $^3H/^3He$), redox indicator species (Mn, Fe, and in situ field O_2), dissolved organic carbon (DOC), and routine N species ($NO_2^- + NO_3^-$, NO_2^-, NH_4^+, Kjeldahl N). In this paper, only in-situ field O_2 data were used. Although samples were analyzed for both $NO_2^- + NO_3^-$ and NO_2^-, NO_2^- concentrations were low and we refer to $NO_2^- + NO_3^-$ as NO_3^-, with the exception of

discussion of N speciation in Fig. 1, where the distinction between $NO_2^- + NO_3^-$ and NO_2^- is made. Dissolved organic nitrogen (DON) was determined by difference between Kjeldahl N and NH_4^+. Total dissolved N (analytically determined for some samples) was not used to estimate DON because of known problems with DON calculations that are based on total dissolved N analyses (Graeber et al., 2012).

Consistent sample collection and processing protocols were used (US Geological Survey, 2011). Samples were collected at the wellhead, upgradient from pressure/holding tanks and treatment systems such as chlorine injection, and without exposure to the atmosphere. Samples for major dissolved gases and environmental tracers were analyzed by methods described at http://water.usgs.gov/lab/. Filtered samples for Mn, Fe, DOC, and the routine N species were analyzed at the USGS National Water Quality Laboratory (http://nwql.usgs.gov/Public/nwql.shtml).

Apparent ages and N_2 data were derived from several sources. Apparent ages, and many of the N_2 data, were compiled by Hinkle et al. (2010). This compilation consisted of environmental tracer and major dissolved gas data collected from Land Use Studies, Major Aquifer Studies, and some reference and miscellaneous wells between 1992 and 2005. Additional N_2 data were compiled from other sources. A description and accounting of these data are provided in the supporting information. Methods used to interpret environmental tracer data were documented in Hinkle et al. (2010). Methods used to quantify N_2 derived from denitrification ("XSN_2") also were documented by Hinkle et al. (2010), and an abbreviated description of the methodology is provided below.
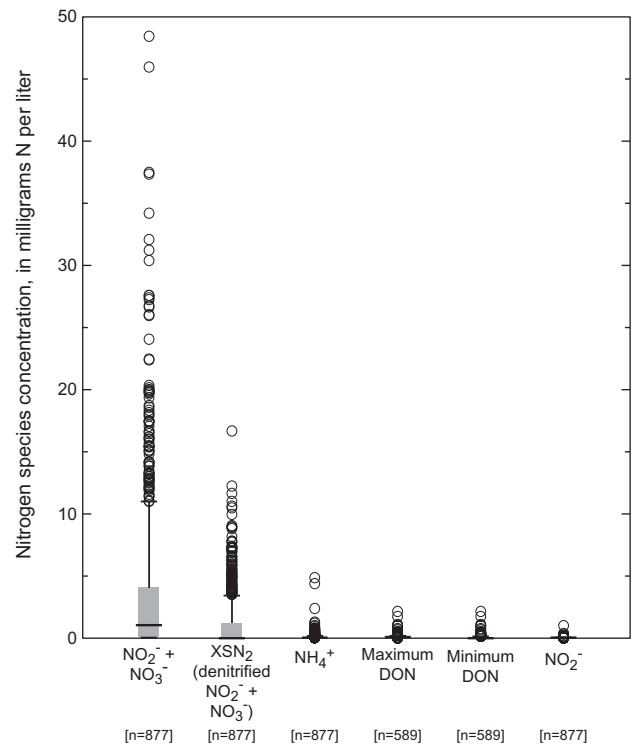

Fig. 1. N concentrations in groundwater ambient-monitoring samples. $NO_2^- + NO_3^-$ is dominated by NO_3^-. Dissolved organic N (DON) calculated as difference between Kjeldahl N and NH_4^+. Kjeldahl N (available for only 589 sites) had high (low-resolution) reporting levels of 0.1 and 0.2 mg N/L; thus, DON distribution bracketed by plotting calculated values for two scenarios: assuming Kjeldahl non-detects = 0.00 mg N/L (minimum DON) and assuming Kjeldahl non-detects present at the reporting levels of 0.1 or 0.2 mg N/L (maximum DON). Non-detects for $NO_2^- + NO_3^-$, NH_4^+, and NO_2^- plotted at one-half of their common reporting levels. Boxplots show inter-quartile range (box), 90th percentile (upper whisker), and outliers (circles).