Journal of Hydrology xxx (2016) xxx–xxx

Contents lists available at ScienceDirect

Journal of Hydrology

journal homepage: www.elsevier.com/locate/jhydrol

Regional oxygen reduction and denitrification rates in groundwater from multi-model residence time distributions, San Joaquin Valley, USA

Christopher T. Green [a,*], Bryant C. Jurgens [b], Yong Zhang [c], J. Jeffrey Starn [d], Michael J. Singleton [e], Bradley K. Esser [e]

[a] U.S. Geological Survey, Menlo Park, CA, USA
[b] U.S. Geological Survey, Sacramento, CA, USA
[c] University of Alabama, Tuscaloosa, AL, USA
[d] U.S. Geological Survey, East Hartford, CT, USA
[e] Nuclear and Chemical Sciences Division, Lawrence Livermore National Laboratory, Livermore, CA, USA

ARTICLE INFO

Article history:
Available online xxxx

Keywords:
Oxygen reduction
Denitrification
Groundwater
Residence time
Multi-model analysis
Regional water quality

SUMMARY

Rates of oxygen and nitrate reduction are key factors in determining the chemical evolution of groundwater. Little is known about how these rates vary and covary in regional groundwater settings, as few studies have focused on regional datasets with multiple tracers and methods of analysis that account for effects of mixed residence times on apparent reaction rates. This study provides insight into the characteristics of residence times and rates of O_2 reduction and denitrification (NO_3^- reduction) by comparing reaction rates using multi-model analytical residence time distributions (RTDs) applied to a data set of atmospheric tracers of groundwater age and geochemical data from 141 well samples in the Central Eastern San Joaquin Valley, CA. The RTD approach accounts for mixtures of residence times in a single sample to provide estimates of in-situ rates. Tracers included SF_6, CFCs, ^3H, He from ^3H (tritiogenic He), ^{14}C, and terrigenic He. Parameter estimation and multi-model averaging were used to establish RTDs with lower error variances than those produced by individual RTD models. The set of multi-model RTDs was used in combination with NO_3^- and dissolved gas data to estimate zero order and first order rates of O_2 reduction and denitrification. Results indicated that O_2 reduction and denitrification rates followed approximately log-normal distributions. Rates of O_2 and NO_3^- reduction were correlated and, on an electron milliequivalent basis, denitrification rates tended to exceed O_2 reduction rates. Estimated historical NO_3^- trends were similar to historical measurements. Results show that the multi-model approach can improve estimation of age distributions, and that relatively easily measured O_2 rates can provide information about trends in denitrification rates, which are more difficult to estimate.

Published by Elsevier B.V.

1. Introduction

Reactions of NO_3^- and O_2 are critical factors affecting water quality and geochemical processes in groundwater (NRC, 2000). Denitrification and oxygen reduction are closely linked and are primary reactions affecting variations of redox chemistry in shallow groundwater (e.g., Vogel et al., 1981; Mariotti et al., 1988; Böttcher et al., 1990; Smith et al., 1991; Mengis et al., 1999; Böhlke et al., 2002; Groffman et al., 2006; Rivett et al., 2008; Green et al., 2008b, 2010; McMahon et al., 2008; Liao et al., 2012). The processes directly affect concentrations of NO_3^-, with broad implications for human and environmental health (Hallberg, 1986; Burt et al., 1993; Fan and Steinberg, 1996; Böhlke, 2002; Hatfield and Follett, 2008; Dubrovsky et al., 2010). In addition, the presence of high NO_3^- concentrations typically indicates the zone of influence of modern agricultural or waste water that can carry other anthropogenic contaminants and can affect the mobility of in-situ contaminants such as uranium and arsenic (Smedley and Kinniburgh, 2002; Jurgens et al., 2010). Rigorous characterization of the fate and transport of NO_3^- and O_2 is therefore essential to managing a range of water quality issues.

Much of the current understanding of oxygen reduction and denitrification in aquifers stems from local studies involving analysis of groundwater samples. After recharge, aqueous concentrations of O_2 typically decrease via microbially mediated reactions with electron donors such as organic carbon or reduced iron or sulfur compounds. After O_2 is depleted, NO_3^- undergoes a series

* Corresponding author.
E-mail address: ctgreen@usgs.gov (C.T. Green).

http://dx.doi.org/10.1016/j.jhydrol.2016.05.018
0022-1694/Published by Elsevier B.V.

Please cite this article in press as: Green, C.T., et al. Regional oxygen reduction and denitrification rates in groundwater from multi-model residence time distributions, San Joaquin Valley, USA. J. Hydrol. (2016), http://dx.doi.org/10.1016/j.jhydrol.2016.05.018

of denitrification reactions with electron donors that ultimately produce N_2. This pattern of reactivity has been observed in local-scale in-situ reactors (Korom et al., 2005) and in flowpath studies of well transects, typically at scales of a few km or less (e.g. Böhlke and Denver, 1995; Singleton et al., 2007; Tesoriero et al., 2007; Green et al., 2008b; McMahon et al., 2008; Welch et al., 2011; Young et al., 2013) that use tracers of chemistry (such as dissolved N_2), recharge conditions (noble gases), and residence time (atmospheric tracers). Challenges remain to connect the findings of local-scale studies to regional observations that are key to understanding the importance of O_2 reduction and denitrification for regional water quality (Otero et al., 2009; Menció et al., 2011; Landon et al., 2011; Refsgaard et al., 2014) and for synthesis across landscapes (Seitzinger et al., 2006).

Recent studies have compared results of local studies toward the goal of identifying common features of nitrate and oxygen reactivity (Tesoriero and Puckett, 2011; Liao et al., 2012). Because solid phase electron donors from lithologic sources tend to limit reaction rates (Green and Bekins, 2010; Tesoriero and Puckett, 2011), the reaction kinetics, especially as regulated by concentrations of O_2 and NO_3^-, are not well known. Zero or first order formulations have been commonly used for simple rate estimates, in lieu of evidence for the applicability of more complex kinetic models. Tesoriero and Puckett (2011) analyzed O_2 and NO_3^- reduction rates at 12 sites across the USA using apparent ages (assuming piston flow) from tracer concentrations to estimate zero order and first order rates of O_2 reduction and denitrification. They found that reaction rates varied over orders of magnitude among sites. Liao et al. (2012) analyzed tracers at 14 sites across the USA using a vertical flux model with a simplified representation of unsaturated and saturated hydrology. They found that zero order O_2 and NO_3^- reaction rates tended to correlate, and that reaction rates were a key factor in determining the eventual steady-state depth of the nitrate fronts. These previous comparisons of local-scale studies indicate that O_2 and NO_3^- reduction rates may be related, but no studies to our knowledge have quantified and compared O_2 and NO_3^- reaction rates in a residence time distribution (RTD) framework for a large agricultural region. One of the goals of this study is to fill this knowledge gap.

Mixing of residence times in groundwater samples poses a challenge for regional characterization of O_2 reduction and denitrification rates. Regional studies typically rely on existing water supply wells with long screens that may produce waters with broad mixtures of residence times from different depths (Landon et al., 2010b). In addition to effects of well construction, geological heterogeneity creates mixed samples even in short screened monitoring wells. Green et al. (2010) found that such mixing of residence times can cause apparent rates derived from groundwater samples to differ from actual local rates by an order of magnitude or more. Improving the accuracy of rate estimates therefore requires methods that account for ranges of residence times and reaction times in a single sample.

A common approach to estimate RTDs in groundwater samples is to apply analytical RTD (also known as "lumped parameter") models. Numerous mathematical forms of the RTD solutions are available (Maloszewski and Zuber, 1982; Visser et al., 2013; Green et al., 2014; Marçais et al., 2015). Comparisons of numerical test cases to various analytical solutions, however, indicate that it can be difficult to determine the form of the RTD a-priori from well construction and aquifer information (Green et al., 2014). It may be advantageous, therefore to consider a range of forms of the RTD in analyzing tracer data along with methods such as multi-model averaging. Consideration of multiple conceptual models of aquifers can minimize bias in predictions (e.g., Troldborg et al., 2007; Rojas et al., 2010). Efforts are ongoing to evaluate the ability of various model-averaging approaches to improve groundwater-model structural adequacy and to reduce prediction errors (e.g., Diks and Vrugt, 2010; Rojas et al., 2010; Ye et al., 2010; Seifert et al., 2012; Refsgaard et al., 2012; Foglia et al., 2013). Use of multi-model averaging has not been explored, to our knowledge, in the use of RTD models calibrated to tracer data. In this study we implement methods of analysis that involve multiple possible RTDs, and we test multi-model averaging as an approach for generating RTDs.

The main objective of this work is to test the hypothesis that denitrification rates relate to O_2 reduction rates in a regional context. We estimated rates of reactions of O_2 reduction and denitrification using a multi-model RTD framework applied to a regional dataset of tracers from the Central Valley, California. Multi-model approaches were tested and applied to reduce errors in estimated RTDs. Automatic parameter estimation techniques were used to determine the most likely values and uncertainties of rate parameter estimates. Rates were summarized in composite distributions based on estimated values and uncertainties, and were compared between O_2 and NO_3^- reduction. The final RTD and reaction models were used to estimate trends in historical NO_3^- concentrations and were compared to observations. The results indicate that the multi-model RTD approach provides a robust and computationally efficient method for estimating NO_3^- reactivity and trends in a regional context.

2. Materials and methods

The procedures to estimate residence time distributions and reaction parameters are shown in Fig. 1. For each groundwater sample, four RTD models were calibrated to the age tracer concentrations (tritium, ^3H; tritiogenic helium, $^3He_{trit}$; terrigenic helium-4, $^4He_{terr}$; carbon-14, ^{14}C; chlorofluorocarbons, CFC-11, CFC-12, and CFC-113; and sulfur hexafluoride, SF_6). The four predicted RTDs for each well sample were then combined into a single multi-model RTD using multi-model averaging techniques. To estimate input histories of NO_3^-, and oxygen reduction and denitrification reaction parameters, each multi-model RTD was combined with input function of NO_3^- and O_2, and the resulting mathematical model was calibrated to observed concentrations of O_2, NO_3^-, and $N_{2,D}$. This approach builds on existing techniques for use of residence time

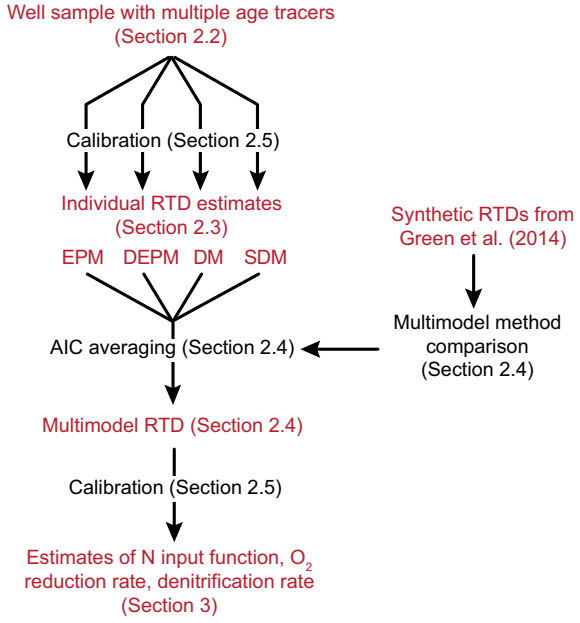

Fig. 1. Schematic of methods, including stages of the estimation procedure (red text) and procedures (black text and arrows). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Please cite this article in press as: Green, C.T., et al. Regional oxygen reduction and denitrification rates in groundwater from multi-model residence time distributions, San Joaquin Valley, USA. J. Hydrol. (2016), http://dx.doi.org/10.1016/j.jhydrol.2016.05.018

Download English Version:

https://daneshyari.com/en/article/5770955

Download Persian Version:

https://daneshyari.com/article/5770955

Daneshyari.com