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Nitrate vulnerability projections from Bayesian inference of multiple groundwater age tracers

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SUMMARY

Nitrate is a major source of contamination of groundwater in the United States and around the world. We tested the applicability of multiple groundwater age tracers (^{3}H, ^{3}He, ^{4}He, ^{14}C, ^{13}C, and ^{85}Kr) in projecting future trends of nitrate concentration in 9 long-screened, public drinking water wells in Turlock, California, where nitrate concentrations are increasing toward the regulatory limit. Very low ^{85}Kr concentrations and apparent $^{3}H/^{3}He$ ages point to a relatively old modern fraction (40–50 years), diluted with pre-modern groundwater, corroborated by the onset and slope of increasing nitrate concentrations. An inverse Gaussian–Dirac model was chosen to represent the age distribution of the sampled groundwater at each well. Model parameters were estimated using a Bayesian inference, resulting in the posterior probability distribution – including the associated uncertainty – of the parameters and projected nitrate concentrations. Three scenarios were considered, including combined historic nitrate and age tracer data, the sole use of nitrate and the sole use of age tracer data. Each scenario was evaluated based on the ability of the model to reproduce the data and the level of reliability of the nitrate projections. The tracer-only scenario closely reproduced tracer concentrations, but not observed trends in the nitrate concentration. Both cases that included nitrate data resulted in good agreement with historical nitrate trends. Use of combined tracers and nitrate data resulted in a narrower range of projections of future nitrate levels. However, use of combined tracer and nitrate resulted in a larger discrepancy between modeled and measured tracers for some of the tracers. Despite nitrate trend slopes between 0.56 and 1.73 mg/L/year in 7 of the 9 wells, the probability that concentrations will increase to levels above the MCL by 2040 are over 95% for only two of the wells, and below 15% in the other wells, due to a leveling off of reconstructed historical nitrate loadings to groundwater since about 1990.

1. Introduction

Rising nitrate concentrations in public supply wells present a serious threat to drinking water in California where wide-spread, long-term application of fertilizers is implicated as the primary cause of nitrate contamination to groundwater (Esser et al., 2002; Harter, 2012). In many key groundwater basins in California, a majority of deep supply wells have nitrate concentrations that are presently above natural, background levels but below the United States Environmental Protection Agency (USEPA) regulatory limit of 45 mg/l (as NO_3^-) (Belitz et al., 2015). The likelihood that nitrate resides in the vadose zone and shallow aquifer zones, but will gradually be transported to deeper aquifers, makes prediction of future trends in nitrate concentration of paramount interest. Long-screened public supply wells tend to capture a broad distribution of groundwater age and in many settings the age distribution determines the evolution of nitrate concentrations in produced groundwater (MacDonald et al., 2003; Wassenaar et al., 2006). Wells exhibiting very young apparent groundwater age are expected to show a rapid response to nitrate applications at the surface. Wells with intermediate ages may show a slower response and long term upward trends, which could continue upward for decades regardless of changes in land use or rates of fertilizer application. Wells dominated by old age distributions could show continued dilution of nitrate by water that is low in

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nitrate, allowing the possibility that wells will continue to produce water below the regulatory limit in the long term.

Methods for detecting and extrapolating trends in nitrate concentrations (Visser et al., 2009b) range from statistical regression based on historical trends (Batlle-Aguilar et al., 2007; Broers and Van der Grift, 2004; Stuart et al., 2007), to use of mass balance based on known loading of N at the surface (Lamontagne, 2002), to mass-transfer functions (Pinault and Dubus, 2008), to simple-one dimensional flow models of downward transport at individual sites (Young et al., 1976) or aggregated groundwater bodies as a whole (Visser et al., 2009a), to application of groundwater flow and transport models that include nonpoint source pollutants and macrodispersivity (Kourakos et al., 2012; Orban et al., 2010). Böhlke and Denver (1995) used groundwater dating, supported by isotopic measurements of nitrate and dissolved gas analysis, to relate observed nitrate trends to historical nitrate application and denitrification. Groundwater dating has since been applied in many cases to aid trend detection and extrapolation (Burow et al., 2007; MacDonald et al., 2003; Wassenaar et al., 2006). Tesoriero et al. (2007) applied groundwater tracer-based ages and redox indicators in a series of wells along flow-paths in four settings to assess the fate and transport of nitrate and other nonpoint source pollutants and showed that increases in nitrate concentrations in groundwater are related to increases in fertilizer applications that took place after about 1960. Visser et al. (2007b) demonstrated that such upward trends in concentrations of nitrate and other related agricultural contaminants have been reversed by legislation limiting nitrate loadings at the national and European level.

Three factors control trends in concentrations of diffuse contaminants at wells: (1) historical inputs, (2) travel times to the well, and (3) geochemical reactions along the groundwater flow path. One approach to projecting the trends in nitrate concentration in water supply wells is to combine statistical reconstructions of nitrate inputs with inferred travel time distributions from recharge to the well. However, the travel time distribution from recharge to the well cannot be measured directly (Massoudieh and Ginn, 2011) and is often described using mathematical lumped parameter models (LPMs) prescribing its shape (Maloszewski and Zuber, 1993, 1998) fitted to measured concentrations of a number of tracers (Åkesson et al., 2014; Corcho Alvarado et al., 2007; Lehmann et al., 2003; Plummer et al., 2001; Solomon et al., 2010; Sültenfuß et al., 2011; Visser et al., 2013b). Recently, non-parametric groundwater age distributions have been derived from age tracers that, unlike the LPMs, have no prescribed shape (Liao et al., 2014; Massoudieh et al., 2014; McCallum et al., 2014; Visser et al., 2013a).

With the LPM representing the travel time distribution from recharge zone to receiving wells and knowing the historical trend of nitrate concentrations in recharging groundwater and the overall rates of nitrate transformations, the future trend of nitrate in the wells can be projected. However, when using environmental tracers to infer the parameters of LPMs, there are multiple sources of uncertainty that propagate into the projection of nitrate trends (Green et al., 2014). These uncertainties include those associated with measured tracers (due to both sampling and analytical methods), representativeness of the samples due to spatial and temporal heterogeneity, uncertainty due to non-conservative tracer transport, making the apparent age of tracers different than the age of water, uncertainty in tracer concentrations at the time of recharge, and most importantly, model structural error due to the fact that the applied LPM is at best a simplification of the real residence time distribution. To obtain a reliable projection, these uncertainties need to be incorporated into the analysis.

For nitrate, the possibility of reactive transport (i.e., denitrification) along the groundwater flow path needs to be ruled out or explicitly modeled (Liao et al., 2012). While the effect of denitrification on groundwater nitrate flux has been found to be limited in some areas (Green et al., 2008a, 2008b), estimating denitrification rates in groundwater bodies is complicated due to mixing along flow paths (Green et al., 2010) and at the well (Green et al., this issue). Dissolved N_2 produced by denitrification is a direct measure of saturated zone denitrification (Singleton et al., 2007; Vogel et al., 1981), while a shift in oxygen and nitrogen isotopes of nitrate is an indication of denitrification in both the unsaturated and saturated zone (Mariotti et al., 1988; McNab et al., 2007).

Bayesian inference has been demonstrated to be a powerful method to perform inverse uncertainty propagation for age distribution modeling (Massoudieh et al., 2012, 2014). Instead of providing single value estimates of the model parameters, Bayesian inference provides the joint probability distributions of the estimated values for the parameters of the groundwater age distributions. Massoudieh et al. (2012) evaluated the appropriateness of several different LPM forms in reproducing the measured tracers using two different measures of goodness of fit including Bayes Factors and Deviance Information Criteria (DIF). Massoudieh et al. (2014) evaluated the information content of temporal measurement of tracers and compared it with single snapshots and showed that in certain cases, having multiple samples collected at large time intervals can provide additional confidence in the estimated LPMs. These studies applying Bayesian inference have relied only on age tracers to derive the age distribution. The Bayesian inference framework can be extended to include nitrate and to project an ensemble of future nitrate trends in drinking water production wells. Historical time series of measured nitrate concentrations can further be included in the Bayesian framework to support the groundwater age distribution. Bayesian inference reveals non-uniqueness and correlations between the parameters and provides an assessment of the information content of both the tracers and other sources of data that are included.

In this study, public supply wells from Turlock, CA, where nitrate concentrations are rising, were sampled for multiple age tracers. Multiple tracers were applied to characterize differently-aged groundwater components in an effort to constrain the age distribution to the extent possible using one-time observations. A number of age tracers are suitable at the time-scale relevant for well vulnerability and response (years to decades): ^{85}Kr (Althaus et al., 2009; Smethie et al., 1992), tritium–helium (Poreda et al., 1988; Schlosser et al., 1988), chlorofluorocarbons (Busenberg and Plummer, 1992), sulfur–hexafluoride (Busenberg and Plummer, 2000), and ^{39}Ar (Loosli, 1983; Loosli et al., 1989; Oeschger et al., 1974). In addition, terrigenic helium (Marine, 1979) typically used for groundwater age dating in the range of 10^3–10^6 years, and ^{14}C, limited to dating groundwater up to approximately 40,000 years due to its 5730 year half-life, can be used to distinguish the contribution of an old, pre-modern, nearly nitrate-free groundwater component diluting the modern fraction. For this study, a combination of ^{85}Kr, ^{3}H, tritiogenic ^{3}He, terrigenic ^{4}He and δ^{13}C and ^{14}C were applied. Age tracer results and nitrate concentration history at the wells are modeled in a Bayesian statistical framework in order to forecast future nitrate concentrations along with estimates of confidence intervals for the predictions at each well. Groundwater age distribution and nitrate concentrations were modeled based on tracer data, nitrate time series, and a combination of tracer data and nitrate time series. The results are discussed with respect to information content of the data sources and the ability to reliably project trends in future nitrate concentrations and the probability of future nitrate concentrations exceeding the USEPA MCL of 45 mg/L as nitrate This is the first study to include nitrate data as an objective of the age distribution and nitrate prediction model framework. Additional analyses (dissolved nitrogen, oxygen and noble gases, and isotopes of nitrogen and oxygen

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