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Research papers

Using environmental tracers to determine the relative importance of travel times in the unsaturated and saturated zones for the delay of nitrate reduction measures

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ABSTRACT

Groundwater quality in many regions with intense agriculture has deteriorated due to the leaching of nitrate and other agricultural pollutants. Modified agricultural practices can reduce the input of nitrate to groundwater bodies, but it is crucial to determine the time span over which these measures become effective at reducing nitrate levels in pumping wells. Such estimates can be obtained from hydrogeological modeling or lumped-parameter models (LPM) in combination with environmental tracer data. Two challenges in such tracer-based estimates are (i) accounting for the different modes of transport in the unsaturated zone (USZ), and (ii) assessing uncertainties. Here we extend a recently published Bayesian inference scheme for simple LPMs to include an explicit USZ model and apply it to the Dünnerngäu aquifer, Switzerland. Compared to a previous estimate of travel times in the aquifer based on a 2D hydrogeological model, our approach provides a more accurate assessment of the dynamics of nitrate concentrations in the aquifer. We find that including tracer measurements ($^{3}H/^{3}He$, ^{85}Kr, ^{39}Ar, ^{4}He) reduces uncertainty in nitrate predictions if nitrate time series at wells are not available or short, but does not necessarily lead to better predictions if long nitrate time series are available. Additionally, the combination of tracer data with nitrate time series allows for a separation of the travel times in the unsaturated and saturated zone.

1. Introduction

Rising nitrate concentrations are negatively impacting the quality of drinking water around the world. In some cases, production wells are ultimately abandoned (e.g. Alikhani et al., 2016); in others, agricultural management practices are changed to reduce the input of nitrate (e.g. Bailey et al., 2015; Hansen et al., 2011; Wassenaar et al., 2006). Due to the costs involved with such nitrate reduction measures, it is important to assess their effectiveness. Such assessments entail not only an estimation of the nitrate reduction potential, but also an estimation of the time lag between implementation of the measures and the decrease of nitrate concentrations in the pumping wells. This time lag is determined mainly by the travel time of water from the point(s) of recharge to the pumping well (Böhlke, 2002; Böhlke and Denver, 1995). Under ideal conditions, this time lag can be determined by comparing observed nitrate concentrations in wells and historical inputs of nitrate into groundwater. However, measured nitrate time series in wells are often too short, the nitrate input history is not known well enough, or other processes affect the nitrate concentrations, such as denitrification (see e.g. Alikhani et al., 2016) or dilution with water that is low in nitrate (e.g. Baillieux et al., 2014). Thus, in most cases, travel times of groundwater, as well as these additional processes affecting nitrate are determined by means of hydrogeological modeling (2D or 3D) and particle tracking, environmental tracers, or a combination of both (Alikhani et al., 2016; Green et al., 2008; Jeffrey Starn et al., 2014; Kaown et al., 2009; MacDonald et al., 2003; McMahon et al., 2006; Osenbrück et al., 2006; Visser et al., 2009; Wang et al., 2012; Zoellmann et al., 2001).

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Environmental tracers are a complementary tool to hydrogeological models and time series of nitrate or other tracers for determining travel time distributions (or age distributions) of groundwater and dilution (Turnadge and Smerdon, 2014; Visser et al., 2009). Measurements of $\delta^{18}O$, SF_6, ^3H, ^{85}Kr, CFCs, ^{39}Ar, ^{14}C, or ^4He are commonly interpreted with lumped-parameter models (LPM) to obtain travel time distributions: The concentrations of the tracers in a well are calculated as the convolution integral of the input history of the tracers and a relatively simple shape of the age distribution (Zuber and Maloszewski, 2001). These shapes can be described by one to just a few parameters (fitted to best reproduce measured concentrations of the environmental tracers) and their pre-selection is often based on the hydrogeological characteristics of the studied area (Cook and Böhlke, 2000). Knowing the age distribution and the nitrate input history can help reconstruct nitrate concentrations in a given well in the past and predict how they will evolve in the future. Alternatively, the nitrate input history can be reconstructed from measured nitrate time series in combination with the age distribution (Visser et al., 2007). Two current difficulties for such assessments are that (i) there is a lack of environmental tracers that can reliably determine travel times of water in the unsaturated zone and (ii) very few studies to date have included a rigorous assessment of the uncertainties associated with the determined age distributions and predictions of nitrate concentrations (Alikhani et al., 2016).

In the unsaturated zone (USZ), nitrate is transported in the water phase, while most environmental tracers are predominately transported in the gas phase, with the exception of ^2H, ^3H, and ^{18}O, which are part of the water molecule itself. Because the two modes of transport have different velocities, travel times for nitrate and environmental tracers from the surface to the well are different, especially if the USZ is thick. Because diffusive transport of gaseous tracers in the USZ is typically faster than the advective transport in the water phase, the USZ is often neglected for gaseous tracers (Zoellmann et al., 2001), i.e. the travel time estimated with these tracers is assumed to represent the travel time in the saturated zone (SZ) only. However, for aquifers with a thick USZ, the travel time of water – and thus nitrate – in the USZ can be a significant portion of the total travel time to the well (Sousa et al., 2013; Wang et al., 2012) and several studies have pointed out that it is problematic to ignore thick USZs (>10 m, Johnston et al., 1998; Schwientek et al., 2009; Zoellmann et al., 2001). To our knowledge, a study by Osenbrück et al. (2006) is the only study that has considered the time lag of gaseous tracers in the USZ (for CFCs) in conjunction with predicting the evolution of nitrate concentrations, but they provided only a limited assessment of the uncertainty of their results.

Several sources of uncertainty need to be assessed when determining age distributions and predicting nitrate concentrations. These include but are not limited to (i) uncertainty in defining a suitable conceptual model of the system (Bredehoeft, 2005), (ii) uncertainty of the tracer measurements, and (iii) uncertainty in additional aquifer parameters that are needed to calibrate models or estimate the time lag in the USZ for example. While uncertainties of tracer measurements are often reported, the resulting uncertainties in estimated parameters, age distributions, mean ages, and predicted nitrate concentrations are rarely calculated rigorously. Approaches to deal with uncertainty typically include sensitivity calculations and calculations of how quickly the goodness of fit decreases for a change in a parameter value (e.g. Corcho Alvarado et al., 2007; Onnis, 2008; Schwientek et al., 2009) and comparing results for different LPMs or different tracers with each other (Corcho Alvarado et al., 2007; e.g. Johnston et al., 1998; Osenbrück et al., 2006). Green et al. (2014) assessed the bias due to model selection and found that, while the obtained age distributions can be very different for different models, they tend to produce similar mean ages and even more similar predictions of solute concentrations, implying that uncertainty associated with model selection is of minor importance for the prediction of the evolution of nitrate concentrations. A new Bayesian modeling approach to estimate age distributions and their uncertainties resulting from measurement errors and additional model parameters in a more rigorous way was introduced by Massoudieh et al. (2012) and applied and extended in two follow-up studies of relatively simple systems (Alikhani et al., 2016; Massoudieh et al., 2014).

In this study, we measured multiple environmental tracers and nitrate to estimate age distributions and predict nitrate concentrations with the Bayesian statistical framework of Alikhani et al. (2016) in an aquifer with a thick unsaturated zone. Multiple pumping wells and piezometers in the Dünnerngäu, Solothurn, Switzerland, were sampled to determine how quickly already implemented nitrate reduction measures will result in a trend reversal of nitrate concentrations. Multiple tracers were used to characterize the groundwater age distribution on a time scale of a few years to decades: ^3H, tritiogenic ^3He (Poreda et al., 1988; Schlosser et al., 1988), radiogenic ^4He (e.g. Torgersen and Stute, 2013), ^{85}Kr (Althaus et al., 2009; Loosli et al., 2000; Smethie et al., 1992) and ^{39}Ar (Loosli, 1983; Loosli et al., 2000). The Bayesian statistical framework of Alikhani et al. (2016) allows us to estimate confidence intervals for the age distributions and predicted nitrate concentrations. Due to the thick USZ of the study area, a special focus is given to the role of the USZ, which is explicitly included in the LPM. Measurements in the USZ were performed to corroborate our model of the USZ. Results are discussed with respect to the effect that explicitly including the USZ in the LPM has on the estimated age distributions and modeled nitrate concentrations. Furthermore, we assess the relative importance of tracer measurements and nitrate time series to obtain reliable and accurate estimates. Finally, the combination of several environmental tracers, including ^3H, with the nitrate time series enables us to estimate the travel times in the unsaturated and saturated zones separately.

2. Study area

The Dünnerngäu aquifer, located in the Canton of Solothurn, Switzerland, is an important source of drinking water in an intensely farmed region of the Central Lowlands of Switzerland affected by high nitrate concentrations. The main crops are grains, corn, potatoes, vegetables, and hay. Extensive application of mineral fertilizer and manure led to increasing nitrate concentrations in leachate and ultimately in groundwater in the 80s and 90s. Nitrate concentrations today are generally above the environmental quality target of 25 mg/L set by the Swiss legislation and even close to the Swiss tolerance value for drinking water of 40 mg/L at some of the wells (Fig. 1). In 1999, the Canton of Solothurn initiated a program of nitrate reduction measures in order to meet the water quality targets for drinking water; primarily by adapted cultivation techniques and secondarily by transforming cropland to extensive meadows. The area of cropland farmed with adapted cultivation techniques increased steadily until 2010 to approximately 890 ha and by then 120 ha of cropland had been converted to extensive meadows (see Fig. A1 in the Electronic Appendix; Hunkeler et al., 2015). Together, this constitutes 89% of the agricultural area in the project perimeter and 26% of the total area of the aquifer (41 km^2). Based on a 2-D particle-tracking model implemented at the start of the nitrate reduction measures in 2000, nitrate concentrations were expected to decrease within a few years of the changes in cultivation (Geotechnisches Institut/TK Consult, 1999). While there was a small initial decrease in nitrate concentrations in the