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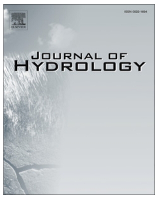

Research papers

New insights into nitrate dynamics in a karst groundwater system gained from in situ high-frequency optical sensor measurements

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ABSTRACT

Understanding nitrate dynamics in groundwater systems as a function of climatic conditions, especially during contrasting patterns of drought and wet cycles, is limited by a lack of temporal and spatial data. Nitrate sensors have the capability for making accurate, high-frequency measurements of nitrate in situ, but have not yet been evaluated for long-term use in groundwater wells. We measured in situ nitrate continuously in two groundwater monitoring wells —one rural and one urban—located in the recharge zone of a productive karst aquifer in central Texas in order to resolve changes that occur over both short-term (hourly to daily) and long-term (monthly to yearly) periods. Nitrate concentrations, measured as nitrate-nitrogen in milligrams per liter (mg/L), during drought conditions showed little or no temporal change as groundwater levels declined. During aquifer recharge, extremely rapid changes in concentration occurred at both wells as documented by hourly data. At both sites, nitrate concentrations were affected by recharging surface water as evidenced by nitrate concentrations in groundwater recharge (0.8–1.3 mg/L) that were similar to previously reported values for regional recharging streams. Groundwater nitrate concentrations responded differently at urban and rural sites during groundwater recharge. Concentrations at the rural well (approximately 1.0 mg/L) increased as a result of higher nitrate concentrations in groundwater recharge relative to ambient nitrate concentrations in groundwater, whereas concentrations at the urban well (approximately 2.7 mg/L) decreased as a result of the dilution of higher ambient nitrate concentrations relative to those in groundwater recharge. Notably, nitrate concentrations decreased to as low as 0.8 mg/L at the urban site during recharge but postrecharge concentrations exceeded 3.0 mg/L. A return to higher nitrate concentrations postrecharge indicates mobilization of a localized source of elevated nitrate within the urbanized area of the aquifer. Changes in specific conductance were observed at both sites during groundwater recharge, and a significant correlation between specific conductance and nitrate (correlation coefficient [R] = 0.455) was evident at the urban site where large (3-fold) changes in nitrate occurred. Nitrate concentrations and specific conductance measured during a depth profile indicated that the water column was generally homogeneous as expected for this karst environment, but changes were observed in the most productive zone of the aquifer that might indicate some heterogeneity within the complex network of flow paths. Resolving the timing and magnitude of changes and characterizing fine-scale vertical differences would not be possible using conventional sampling techniques. The patterns observed in situ provided new insight into the dynamic nature of nitrate in a karst groundwater system.

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1. Introduction

Widespread increases in nitrate concentration in groundwater systems are a global concern because of potential deleterious effects on drinking-water supplies and because groundwater nitrate contributes to the eutrophication of aquatic ecosystems (Nolan et al., 1997; Rabalais et al., 2002; Galloway et al., 2008; Dubrovsky et al., 2010). Karst groundwater systems are particularly susceptible to anthropogenic contamination because recharge may infiltrate directly through conduits, caves, and sinkholes at the land surface and carry contaminants throughout the system (White, 1988; Vesper et al., 2001; Kresic, 2013). Because karst aquifers are characterized by rapid recharge via karst

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features and extensive surface-water/groundwater interaction, geochemical measurements are often used to constrain different components of flow (i.e. recent recharge and movement through diffuse versus conduit flow paths) (Vesper et al., 2001; Musgrove et al., 2010). Continuous monitoring of groundwater levels, spring discharge, and physicochemical properties— such as specific conductance, temperature, and turbidity—provide information about aquifer structure and the timing and magnitude of water movement through the karst matrix as a function of hydrologic conditions (e.g., Hess and White, 1988; Larocque et al., 1998; Massei et al., 2003). Similar detailed information about patterns of nitrate concentration, especially during drought conditions and groundwater recharge events, can provide new insights for identifying short- and long-term patterns, understanding of how groundwater systems respond to changing climatic conditions, and predicting changes to public water supplies.

Resolving temporal and spatial dynamics of nitrate in groundwater systems remains challenging because conventional sampling techniques are time consuming and constrain data collection. For example, groundwater wells often require the use of large pumps for purging and the long purge time (hours) required for a single sample makes the collection of discrete samples expensive and time consuming. With the time for the hydrologist to travel to and from the site factored in, collection of a single sample per day may be all that is possible for many well locations. Consequently, most groundwater monitoring of nitrate is typically at the weekly, monthly, or yearly sampling intervals, all of which are inadequate to resolve temporal changes in rapidly responding groundwater systems such as karst. These problems are compounded when needing to collect samples from a network of wells, thereby limiting the amount of spatial coverage that is possible to resolve patterns across the landscape. Furthermore, laboratory analysis of discrete samples is required, often with long reporting times. Optical nitrate sensors (herein nitrate sensors) have the demonstrated capability for making accurate high-frequency measurements of nitrate in springs, streams, estuaries, and large rivers (Sanford et al., 2007; Heffernan and Cohen, 2010; Pellerin et al., 2012, 2014), but to date, evidence of long-term use in groundwater wells is not apparent in the literature.

In this study, nitrate sensors were evaluated for their ability to resolve temporal and vertical changes in nitrate concentrations in groundwater from the Edwards aquifer, a productive karst aquifer in central Texas (Sharp and Banner, 1997). Instrument accuracy, precision, and error were assessed in laboratory tests. Nitrate sensors were deployed in situ in two groundwater monitoring wells—one rural and one urban—located in the unconfined zone of the Edwards aquifer. Nitrate, specific conductance, and groundwater levels were monitored continuously at hourly intervals for more than a year at the rural and urban wells and included both extreme drought conditions (U.S. Drought Monitor, 2016) and a prolonged period of groundwater recharge. At the rural well, the variability in nitrate concentration and specific conductance with depth, and their relation to vertical flow within the well bore were also examined. Results highlight how high-frequency nitrate data from groundwater settings vary over a range of hydrologic conditions, and provide new insights into the timescales on which groundwater chemistry can change.

2. Hydrologic and climatic setting

The Edwards aquifer is the primary water supply for more than 2 million people, is heavily used for irrigation, and provides critical habitat for threatened and endangered aquatic species at major springs (Sharp and Banner, 1997; Edwards Aquifer Research and Data Center, 2015). The San Antonio segment of the aquifer extends from western Kinney County, Tex. eastward into Hays County, Tex (Fig. 1). The Edwards aquifer consists of lower Cretaceous-aged carbonate rocks that are heavily faulted; extensive dissolution has yielded a porous karst matrix (Barker and Ardis, 1996). The majority of aquifer recharge is in the form of direct infiltration from streams that drain the contributing zone (catchment area) of the Edwards aquifer as they flow across the unconfined recharge zone (Puente, 1978). Aquifer discharge occurs primarily through springs and groundwater withdrawal (pumping). Downgradient of the recharge zone, the aquifer becomes confined and is artesian. The regional flow path of groundwater in the Edwards aquifer is generally west to east from Kinney County through Uvalde, Medina, and Bexar Counties, Tex. (Maclay and Land, 1988; Clark and Journey, 2006). The flow path then shifts northeast through Comal County, Tex. where discharge from the regional flow path occurs at natural springs (Lindgren, 2006; Musgrove and Crow, 2012).

Groundwater-level changes in response to changes in climate and patterns of precipitation are readily apparent in monitoring wells in the unconfined zone of the Edwards aquifer (Musgrove et al., 2010). Rainfall in the San Antonio area averages approximately 74 cm/y (National Oceanic and Atmospheric Administration, 2015a) but varies widely from year to year. Multi-year droughts are common (Bomar, 1994), and water levels often progressively decline during drought owing to low amounts of recharge coupled with continued discharge through springs and pumping. Periods of wet weather also are common, especially in fall and winter or as a result of tropical storms during the summer and fall (Bomar, 1994). Under wet hydrologic conditions, groundwater levels and spring discharge can increase quickly (hours to days) and progressive increases may continue for months.

In this study, groundwater monitoring in wells began in July 2014 when the region was experiencing a prolonged drought (U.S. Drought Monitor, 2016). Major recharging streams had little flow during this period of drought, and groundwater levels and spring discharges were in general decline. In April 2015, an extended period of above average rainfall (National Oceanic and Atmospheric Administration, 2015a) and corresponding aquifer recharge began, fundamentally changing the regional hydrology from drought to relatively wet conditions. Both rapid short-term (hours to days) and more gradual long-term (weeks to months) observations of groundwater recharge and the associated changes in water chemistry were captured during the monitoring period from July 1, 2014 through September 5, 2015.

3. Nitrate in the Edwards aquifer

Water chemistry in the San Antonio segment of the Edwards aquifer is generally well-mixed vertically in the aquifer although a high degree of spatial variability in nitrate and other anthropogenic contaminants is evident regionally (Lindgren, 2006; Musgrove et al., 2014). Since the 1950s, there has been an increase in nitrate concentrations in the Edwards aquifer and this increase has been attributed, at least in part, to anthropogenic loading (Musgrove et al., 2016).Water in the Edwards aquifer is generally oxic (with concentrations above 4 mg/L dissolved oxygen) and dissolved organic carbon concentrations are very low (less than 1 mg/L) resulting in conditions not likely to favor the removal of nitrate by denitrification. Whereas conditions are likely unfavorable for denitrification, the process of nitrification may be an important nitrogen transformation process that increases groundwater nitrate concentrations because nitrification of ammonium and organic nitrogen to nitrate occurs in overlying soils (Einsiedl and Mayer, 2006; Stoewer et al., 2015) and within the aquifer itself (Musgrove et al., 2016).

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