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Dynamics of nitrate and methane in shallow groundwater following land use conversion from agricultural grain production to conservation easement

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ABSTRACT

Fertilizer applications on agricultural fields lead to elevated nitrate concentrations in groundwater. This increases nitrate concentrations in the baseflow of streams, enhancing downstream eutrophication. Conservation practices reduce the impacts from agriculture, but little is documented on the recovery time of shallow groundwater after agriculture ceases and conservation practices are applied. Although conservation practices may reduce groundwater nitrate, they may also lead to the production of the greenhouse gas methane. This study investigated the temporal sequence of applying post-agricultural conservation practices and the effects on nitrate and methane concentrations in shallow groundwater. Harleigh Farms is a complex of fields near Oxford, MD (USA) that have been taken out of crop production and placed in conservation programs at various times after 1997. Groundwater nitrate and dissolved methane were sampled monthly from Nov 2012-Nov 2013 using age of the conservation practice as a proxy for time since fertilization. In this chronosequence study, an exponential decline in groundwater nitrate levels was found over the 16 year time period since last fertilization. Within 3–5 years after the cessation of intensive grain production, groundwater nitrate concentrations in the top of the surface unconfined aquifer dropped from 11 mg NO_3^--N L^{-1} to 0.5 mg NO_3^--N L^{-1}. Methane only accumulated to high concentrations (2–60 μM CH_4) in hydric soils with low nitrate concentrations ($\ll$ 0.1 mg NO_3^--N L^{-1}). Our results indicate rapid loss of nitrate in the top of the surficial aquifer after the cessation of intensive agriculture and seasonal accumulations of methane in wetland-based conservation practices. These data indicate that time series of groundwater nitrate concentrations at the top of the unconfined aquifer can be used to evaluate the effectiveness of agricultural conservation practices.

1. Introduction

A common water quality problem around the world is high nitrate (NO_3^-) in shallow ground and surface waters fueling eutrophication (Davidson et al., 2012). Nitrate, which is bioavailable and soluble, is of particular concern since it moves readily with water. Nitrate is naturally present at low concentrations in soils and water; however, in many places ground and surface water nitrate has increased due to fertilizer application to lawns and crop fields and by discharges of wastewater from sewage plants and septic systems (Valiela and Costa, 1988; Spalding and Exner, 1993; Reay, 2004; Dubrovsky et al., 2010). High nitrate concentrations ($\gg >$ 10 mg NO_3^--N L^{-1}) in freshwater also makes the water unfit for human consumption (Follett and Follett, 2001). Excess nitrate in groundwater-fed streams and rivers (in conjunction with phosphorus) negatively affects water quality by causing eutrophication in downstream lakes and estuaries, providing suitable conditions for harmful algal blooms, loss of submerged aquatic vegetation due to lack of light penetration, and dead zones (Kemp et al., 2005). The Chesapeake Bay and tributaries is a well-studied eutrophic system that is plagued with annual dead zones due to increased N inputs from mixed land uses within its watershed (Kemp et al., 2005; Fisher et al., 2006).

Conservation practices, such as riparian buffers and wetlands are often used to reduce the water quality impacts of fertilizer. These practices enhance biological processes which intercept nitrate within an agricultural landscape (Lowrance et al., 1997). The many efforts underway in the Chesapeake Watershed to reduce the impacts of fertilizer and manure applications on agricultural lands and suburban lawns have yielded few improvements in stream and river water quality (Denver et al., 2004; Dubrovsky et al., 2010). This is primarily considered to be the result of long groundwater residence times of years to decades (e.g., Sanford and Pope, 2013). However, there are relatively few studies

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focused on the recovery time of shallow groundwater after agricultural fields are converted to conservation practices (Primrose et al., 1997; Schilling and Spooner 2006; Tomer et al., 2010; Schilling and Jacobson 2010).

Although land use conversion studies are common (e.g., Foley et al., 2005), conversion from agriculture to grassland has few studies with reference to groundwater nitrate concentrations. Time series and chronosequences (artificial time series using similar sites with varying ages since agricultural usage) have both been used to investigate the changes in groundwater nitrate. For example, a chronosequence study performed in Iowa on land use conversion from agriculture to prairie showed nitrate concentrations decreasing at 0.58 mg NO_3^--N L^{-1} y^{-1} in the top of the unconfined aquifer (Schilling and Jacobson, 2010). A time series analysis of nitrate concentrations in a stream draining the area of the chronosequence study plus additional areas with no land use change showed nitrate decreasing more slowly at 0.12 mg NO_3^--N L^{-1} y^{-1} (Schilling and Spooner, 2006). These studies show large nitrate reductions in groundwater and streams after agricultural retirement in their study region, but the results are limited geographically and are specific to one soil class. If similar rates are found in the Chesapeake Bay region, then groundwater residence time may be a smaller factor in nitrate remediation than insufficient adoption or unknown or increasing nitrate sources.

Nitrate is a serious water quality concern, but one confounding problem with conservation efforts may be the production of the greenhouse gas methane due to changing hydrology and encouraging anaerobic conditions that can induce methanogenesis (Reeburgh, 2007). Besides improving water quality, converting agricultural land back to natural conditions can have impacts on greenhouse gases that accumulate in water (Huttunen et al., 2003; Hendriks et al., 2007; Reeburgh 2007). The Conservation Reserve Program (CRP) and the Conservation Reserve Enhancement Program (CREP) are voluntary USDA programs that remove sensitive land from agricultural production and substitute plants that improve environmental quality (typically warm and cool-season grasses). Areas taken out of farm production under CRP and the CREP are often those lands that tend to collect water, and these areas are easily converted back to wetlands, which are hotspots for both denitrification and methanogenesis, the production of methane (CH_4). Although wetlands aid in processing nitrogen, about 12% of the global production of the greenhouse gas methane comes from wetlands (Reeburgh, 2007). It is well established that methane is the second most important greenhouse gas after carbon dioxide in terms of radiative forcing in the atmosphere. On a molar basis, methane is about 105 times more effective at heating the atmosphere than carbon dioxide over a 20 year period (Shindell et al., 2009; Howarth et al., 2011). The largest contributors of methane emissions are freshwater wetlands and rice production, respectively (Reeburgh, 2007). High levels of methane (up to 20,000 times the atmospheric background) have been detected in groundwater under farm ditches, controlled drainage structures, and wetlands, and these high concentrations could result in ebullition (bubble formation) of methane into the vadose zone and rapid transport to the atmosphere (Fisher et al., 2010; Fox et al., 2014).

One study (Morse et al., 2012) investigated wetland greenhouse gas fluxes after wetland restoration in a former agricultural field in coastal North Carolina. Methane fluxes were found to be highly variable, and the highest fluxes were found in the warm months and at the wettest sites. The wetland sites had significantly higher methane fluxes than the agricultural field, but the agricultural field had higher greenhouse gas fluxes (CO_2-equivalents) due to carbon dioxide and nitrous oxide fluxes (Morse et al., 2012). There appears to be a dual nature to the effects of conversion of active agricultural land to natural or conservation land use. Soil nitrogen declines, groundwater nitrate appears to decrease, and stream nitrate concentrations decrease. However, wetland emissions of greenhouse gases may also increase, posing a potential trade-off between improving water quality and augmenting greenhouse gas emissions. If methane is produced in groundwater at lower concentrations of nitrate, ebullition is a possibility, potentially avoiding methane oxidation in higher, more oxic soil strata.

Methanogenesis is known to be inhibited by the presence of other electron acceptors, such as oxygen (O_2), nitrate, ferric iron (Fe^{3+}), and sulfate (SO_4^{2-}). Iron- and sulfate-reducers outcompete methanogens for substrate (Achtnich et al., 1995a, 1995b), but the reduction of nitrate suppresses methanogenesis by the presence of toxic denitrification intermediates: nitrite (NO_2^-), nitric oxide (NO), and nitrous oxide (N_2O, Roy and Conrad, 1999). In agricultural fields, nitrate is the dominant electron acceptor after oxygen. Although ferric iron and sulfate also inhibit methanogenesis, these electron acceptors are not found in high concentrations in agricultural areas in our study region (Kasper et al., 2015).

The objective of this study was to evaluate the nitrate and methane impacts of applying conservation practices to agricultural land over time. Harleigh Farms in Talbot County, MD represented a unique opportunity to evaluate reductions in agricultural nitrate and potential methane production in groundwater because of the documented retirement of a series of farms from intensive grain production to conservation planting for wildlife. Groundwater nitrate and methane levels in the surficial aquifer were monitored in a chronosequence of plots with as many as 16 years of post-agricultural conservation land use. We wanted to test the concept that if conservation practices are effective, then improvements in groundwater quality should be observable under the practice. The chronosequence reported here provides information on the time period required for groundwater nitrate concentrations to decrease on the coastal plain in Maryland. We hypothesized that nitrate concentrations would decrease as time out of agricultural production increased, and that methane concentrations would increase over time as the supply of the alternate electron acceptor nitrate decreased, resulting in more methanogenesis in the anaerobic metabolism of the soil.

2. Materials and methods

2.1. Study sites

For this chronosequence study, we examined groundwater nitrate and methane concentrations under fields that had been sequentially retired from grain production over 16 years. One field was still in active grain production, and the other six fields were last farmed from 2 to 16 years prior to the start of the study. The varied land retirement history of these fields provided a 16 year chronosequence of groundwater chemistry conditions after the cessation of fertilization. Sampling was conducted monthly from November 2012-November 2013.

This study was conducted at Harleigh Farms, located in Talbot County on the eastern shore of Maryland (Fig. 1). All of the sites drain to the tidal Trippe Creek, a tributary of the Tred Avon River which drains to the Choptank River (the seventh largest tributary to the Chesapeake Bay by catchment size). The site is in the hydrogeomorphic region “fine-grained lowlands” that is characterized by a shallow water table (generally 0 to 3.0 m below land surface) and poorly drained sediments of low permeability (Hamilton et al., 1993). All sites are between 3 and 7 m above sea level. Soil types and the presence of hydric soils were determined using USDA’s SSURGO dataset (Soil Survey Staff, 2017). Due to the limited size of conservation practices at Harleigh Farms, soil type selections were limited. All sites were poorly to somewhat poorly drained, except for the Forest site, which was well drained (Table 1). Forest and agriculture are the two major land uses and represent end members in terms of nitrogen inputs (forests = low, agriculture = high). To provide nitrate data from both well and poorly drained soils outside Harleigh Farms, data from other nearby sites with a range of soil types on Maryland’s Eastern Shore were also used to supplement these forest and agricultural end members of nitrate input (Table 1).

Over the past 17 years, Harleigh Farms has successively acquired fields in intensive grain production (corn, wheat, soy) and put them