

## Nitrogen Contamination of Surficial Aquifers—A Growing Legacy<sup>†</sup>

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### Historic Perspective

Since the end of the Second World War (WWII), there have been increased releases of nitrogen (N) into the environ-

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ment as a result of increased fertilizer usage, fixation by crops, mineralization of animal manure, and atmospheric deposition, along with miscellaneous other sources (1, 2). N contamination is of interest because of potential health effects in drinking water (3, 4), nutrient enrichment of terrestrial (2, 5) and aquatic ecosystems (6), and contributions to global warming (2, 7). From 1945 to 2002 industrially fixed fertilizer N use in the United States increased 20-fold (Figure 1) to about 12 Tg y<sup>-1</sup>, and 78–85 Tg y<sup>-1</sup> globally (2). In addition to inputs of industrially fixed N, animal manure and atmospheric deposition can contribute large amounts as well—up to 8.1 Tg y<sup>-1</sup> across the continental U.S. However, field studies rarely account for more than about 50% of applied N in harvested crops (8) and it is commonly assumed that 30% is lost through runoff or leaching to groundwater as NO<sub>3</sub><sup>-</sup> (7, 9, 10). Owing to the mobility of nitrate (NO<sub>3</sub><sup>-</sup>), groundwater is vulnerable to contamination from leaching; especially shallow unconfined aquifers underlying agricultural lands (3). In addition to contributing to impacts on water quality, this excess NO<sub>3</sub><sup>-</sup> adds uncertainty to estimates of nitrous oxide (N<sub>2</sub>O) emissions, an important greenhouse gas (7, 10).

### Trading Space for Time

Heretofore, assessing historical trends in NO<sub>3</sub><sup>-</sup> contamination of groundwater has been problematic due to the scarcity of long-term NO<sub>3</sub><sup>-</sup> concentration data. However, application of two developments—methods for estimating recharge dates for groundwater and the original NO<sub>3</sub><sup>-</sup> concentrations at the time of recharge (11)—allow reconstruction of the NO<sub>3</sub><sup>-</sup> input history as well as assessment of the potential for removal by denitrification. In most aquifers groundwater moves at very slow rates determined by the properties of the aquifer materials. Travel times of only a few tens of meters per year are common and groundwater residence times may vary from

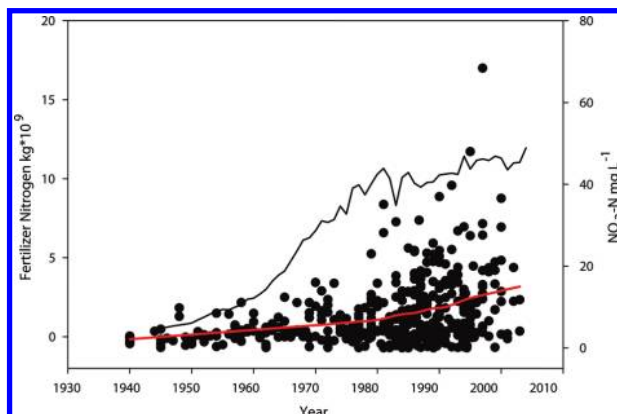
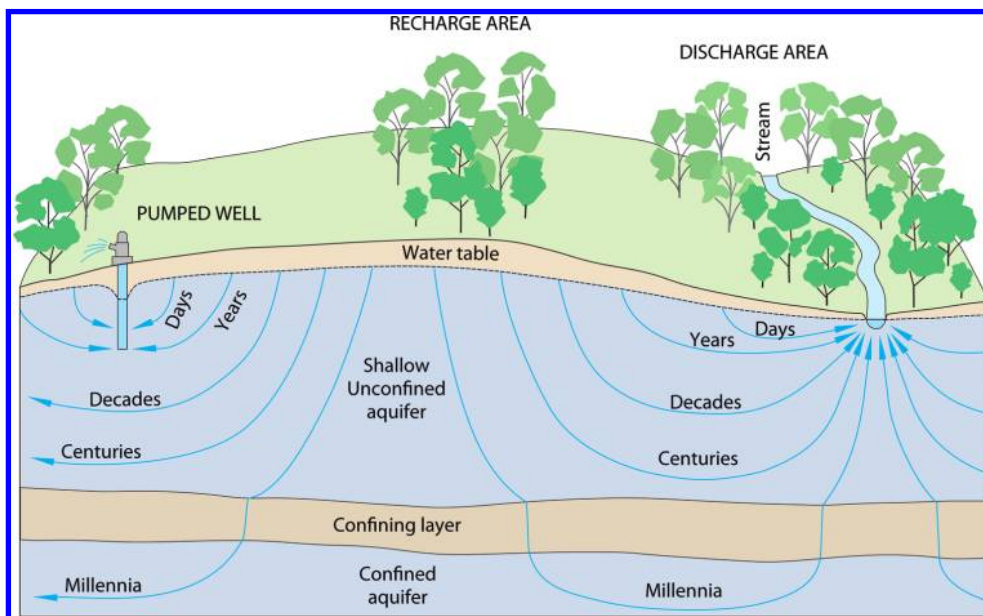
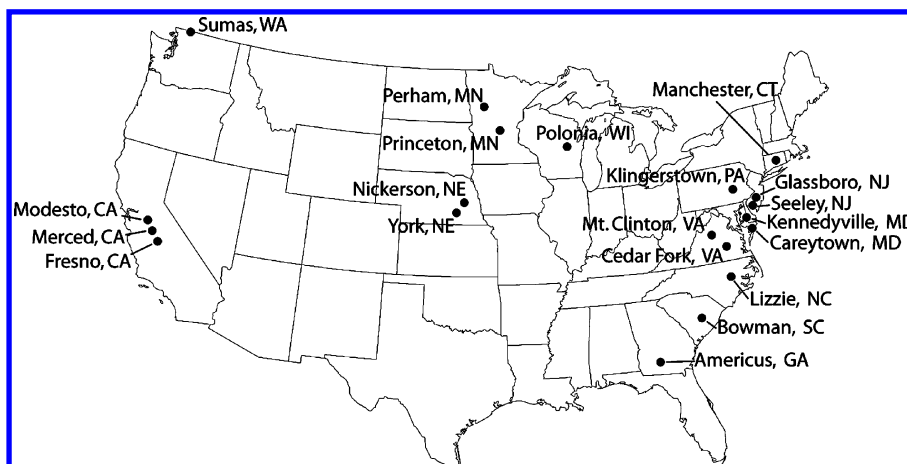


FIGURE 1. Groundwater NO<sub>3</sub><sup>-</sup> concentrations adjusted for denitrification (black circles) for 424 samples from the sites shown in Figure 3, and annual fertilizer N use data (black line) for the U.S. since 1945. A Lowess curve fit to the data (red line) indicates that NO<sub>3</sub><sup>-</sup> concentrations have increased from about 2 mg L<sup>-1</sup> in the early 1940s to about 15 mg L<sup>-1</sup> in 2003.



**FIGURE 2.** Diagram of groundwater flow paths and residence times in typical surficial aquifers; modified after Heath (34). Groundwater travel times vary greatly depending on distance from the recharge area, aquifer hydraulic properties, slope, and depth. Consequently, aquifers comprise a variety of waters of varying age and composition. By sampling at various points on flow paths it is possible to reconstruct a chronology of aquifer contamination.



**FIGURE 3.** Map showing locations of groundwater sampling sites used in this analysis.

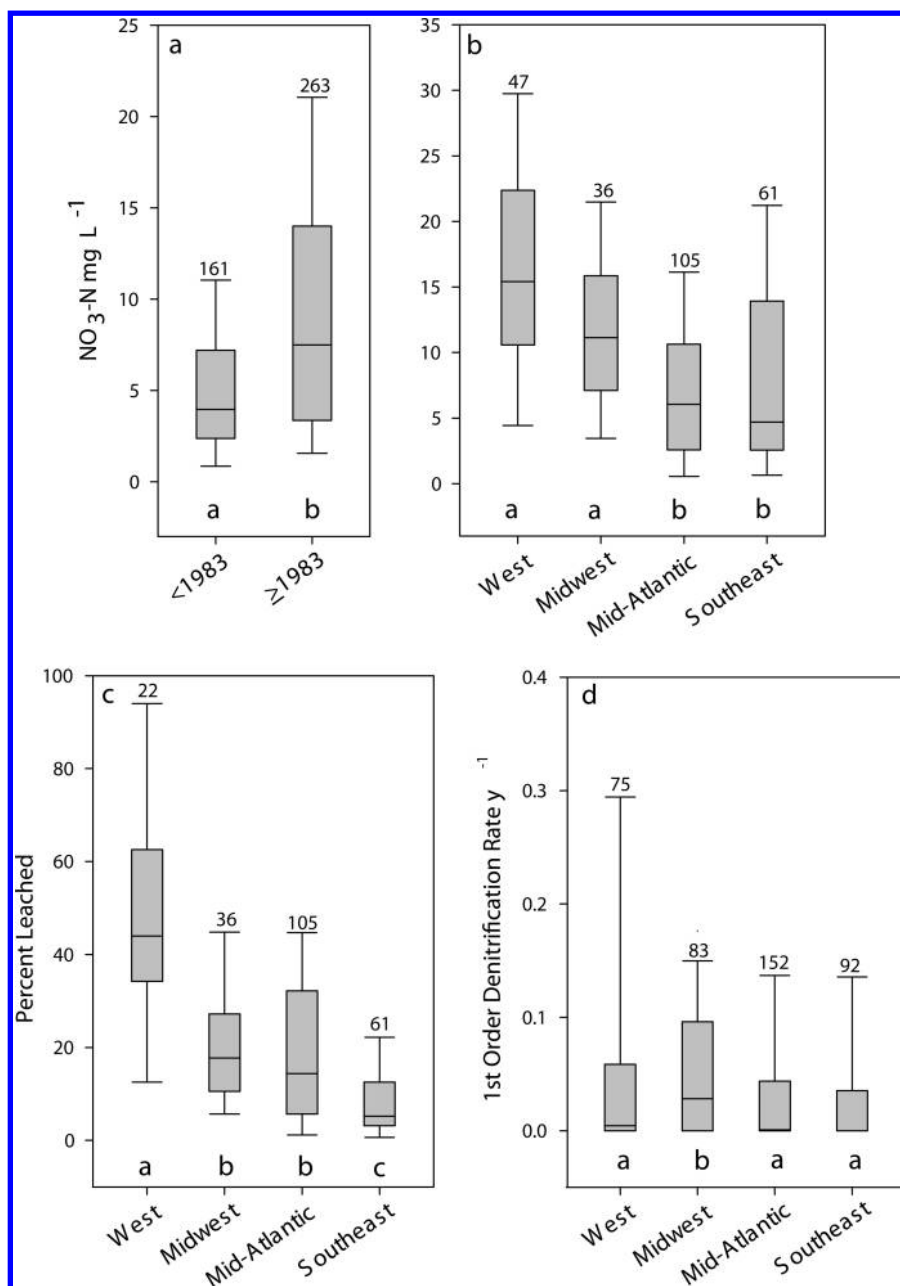
a matter of days near streams and other discharge areas, to centuries for groundwater that recharged at groundwater divides (Figure 2) (12). Therefore most shallow unconfined aquifers contain a cross section of waters of varying ages. By installing well screens at various depths in aquifers, it is possible to measure  $\text{NO}_3^-$  concentrations in samples of groundwater that recharged at various times in the past.

An intrinsic problem faced in quantifying and understanding the impacts of excess  $\text{NO}_3^-$  is that in some aquifers  $\text{NO}_3^-$  losses and trends may be masked due to denitrification (13–15), a microbiological process by which  $\text{NO}_3^-$  is converted to  $\text{N}_2$  gas. Because the  $\text{N}_2$  gas created by denitrification remains in solution (16), it can be used to reconstruct  $\text{NO}_3^-$  concentrations at the time of recharge, making it possible to reconstruct multidecade chronologies of  $\text{NO}_3^-$  contamination from spatially distributed sampling points in aquifers. This space-for-time approach is particularly useful for examining historical  $\text{NO}_3^-$  trends in groundwater, since residence times in surficial aquifers are typically on the same order (12) as the six-decade historical trend of increasing nitrogen inputs. The U.S. Geological Survey (USGS) has sampled groundwater in aquifers across the nation, allowing us to evaluate spatial

and temporal trends of  $\text{NO}_3^-$  contamination. For this analysis we used 424 groundwater samples, age dated and corrected for denitrification, from 20 surficial aquifer studies done throughout the U.S. (Figure 3). These aquifers are in predominately agricultural watersheds, although several include expanding urban areas (Supporting Information (SI), Table S1).

### Temporal and Spatial Patterns of Nitrate in Groundwater

The USGS groundwater samples, corrected for denitrification, provide a historical record showing a clear pattern of increasing  $\text{NO}_3^-$  recharge concentrations in the U.S. since 1945 (Figures 1 and S1). This pattern corresponds to the increase in industrially fixed fertilizer N use in the U.S. during 1945–2002. A Lowess curve fit to the entire data set indicates that  $\text{NO}_3^-$  concentrations increased from about  $2 \text{ mg L}^{-1}$  (Note:  $\text{NO}_3^-$  concentrations are reported in  $\text{mg L}^{-1}$  as N) in the early 1940s to about  $15 \text{ mg L}^{-1}$  for samples that recharged in 2002 (Figure 1). Comparing  $\text{NO}_3^-$  concentrations for the more recent 1983–2002 period with the 1945–1982 period (17) revealed an increase from a median of 4 to  $7.5 \text{ mg L}^{-1}$  ( $P < .001$ ) (Figure 4a). Among



**FIGURE 4.** Comparisons of (a)  $\text{NO}_3^-$  concentrations for the <1983 and  $\geq 1983$  time periods for all 424 samples from the 20 sample locations, (b)  $\text{NO}_3^-$  concentrations for the  $\geq 1983$  time period in the 4 major regions sampled, (c) the percent of applied N that leached to groundwater by region for the  $\geq 1983$  time period, and (d) denitrification rates by region for the entire time period. Sample numbers differ for the western region between panels (b) and (c) because land use and fertilizer data needed for calculations in panel (c) were not available for 2 sites; samples for the single northeastern region site are only included in panel (a). Box plots display the 5th, 25th, 50th, 75th, and 95th percentile; values above the upper whiskers are the number of samples in each category. Boxes having the same lower case letter below them are not significantly different.

the 20 sites,  $\text{NO}_3^-$  concentrations increased significantly by at least  $5 \text{ mg L}^{-1}$  at 11 sites, and 4 of those increased by at least  $10 \text{ mg L}^{-1}$ . Regionally,  $\text{NO}_3^-$  concentrations (Figure 4b) were greatest in the western and midwestern sites (median =  $15.4$  and  $11.1 \text{ mg L}^{-1}$ , respectively), and lowest in the mid-Atlantic and southeastern sites (median =  $6.0$  and  $4.7 \text{ mg L}^{-1}$ , respectively). Estimates of the percent of applied N leaching to groundwater (Figure 4c) were significantly greater in western sites (median =  $43.9\%$ ), moderate in the upper midwest (median =  $17.7\%$ ), and mid-Atlantic (median =  $14.4\%$ ), and lowest in the southeast (median =  $5.2\%$ ). Some of the largest leaching rates (median =  $19.9\%$ ) occurred in irrigated sites, whereas the smallest rates (median =  $4.5\%$ ) were in poorly drained sites with tile drains and ditches. Among sites, leaching

rates varied from  $3.7$  to  $48.5\%$ , with a sample median of  $14\%$  and a site-by-site median of  $18.3\%$  for the  $1983\text{--}2002$  period. These values agree with the  $14.7\%$  employed in a recent global N mass budget (18), and it is important to note that they are about half the  $30\%$  default value recommended by the Intergovernmental Panel on Climate Change (IPCC) (9) for estimating agricultural emissions of  $\text{N}_2\text{O}$ .

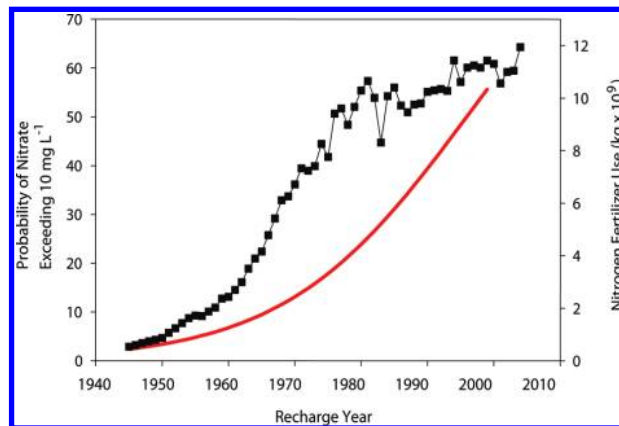
The largest  $\text{NO}_3^-$  concentrations and leaching rates occurred in study areas in the west and midwest in aquifers with intensive agricultural inputs, sandy well-drained soils, and irrigation—all 8 sites west of the Mississippi River were irrigated. The smallest  $\text{NO}_3^-$  concentrations and leaching rates occurred in study areas with tile drains and ditches which were primarily located in the southeast—all but one

of which were not irrigated. A recent USGS study (13) has shown that shallow aquifers are most susceptible to  $\text{NO}_3^-$  contamination in settings with irrigated agriculture and well-drained aquifer materials, whereas they are least susceptible in settings with poorly drained soils. In well-drained soils  $\text{NO}_3^-$  moves quickly to the water table and there is often little time for saturated conditions to develop in the soil zone where denitrification can occur. Another factor potentially controlling  $\text{NO}_3^-$  leaching in irrigated areas is that the fertilizer is often applied at the same time as irrigation water, and in some cases it is dissolved in it (a process called chemigation). Consequently any excess water that leaches to groundwater during the growing season potentially carries a greater  $\text{NO}_3^-$  load than recharge occurring outside the growing season. Poorly drained soils, on the other hand, are typically managed with tile drains and ditches that shunt shallow groundwater directly to surface water carrying much of the excess  $\text{NO}_3^-$  with it, while bypassing normal groundwater flow paths. These poorly drained soils also often contain sufficient organic matter that under saturated conditions supports denitrification, lowering  $\text{NO}_3^-$  concentrations in the limited groundwater recharge that does occur.

In our analysis, the amount of denitrification that occurred was limited in groundwater that recharged since 1983. However, in groundwater that recharged before 1983 a median of 65% of the original  $\text{NO}_3^-$  remained. These results indicate that groundwater <20 y old is especially susceptible to  $\text{NO}_3^-$  contamination and denitrification will do little to eliminate it. Groundwaters >20 y old typically are in portions of aquifers that may be able to remove some or all  $\text{NO}_3^-$  through denitrification. Overall, denitrification rates were low with limited denitrification occurring in 8 of the 20 study areas. For the remaining 12 study areas median first-order denitrification rates ranged from 0.01 to 0.22  $\text{y}^{-1}$  with half-lives ranging from 3.1 to 44.7 y. Our results reinforce the recent finding (19) that the shallow portions of many aquifers lack the conditions required for denitrification and therefore have limited potential for natural bioremediation. These findings suggest that recent global denitrification estimates (15) that assume 30–40% leaching rates and a 2-y half-life for  $\text{NO}_3^-$  in shallow groundwater overestimate the amount of denitrification that occurs in this zone.

### Implications for Water Quality and Health Effects

Globally, groundwater comprises about 99% of available fresh water. As climate change decreases the reliability of surface water systems, populations will turn more to groundwater as a fresh water source. However, as our analysis shows, groundwater is highly vulnerable to contamination. Daily, about  $61 \times 10^9$  L in the U.S. (20) and  $2.2 \times 10^{12}$  L globally (21) is withdrawn from groundwater for public supply. This widespread dependence on a resource susceptible to  $\text{NO}_3^-$  contamination is especially important given that epidemiological studies have linked exposure to  $\text{NO}_3^-$  at concentrations well below Environmental Protection Agency (EPA) and World Health Organization (WHO) standards to several cancers and negative birth outcomes (4).  $\text{NO}_3^-$  concentrations in groundwater typically increase from relatively low concentrations in water that recharged prior to 1960, to values often exceeding the EPA and WHO drinking water standards of 10 and 11.3  $\text{mg L}^{-1}$ , respectively, (4) in water that recharged since 1980 (Figures 1 and S1). For example, in our data 2.2% of samples that recharged prior to 1960 exceeded the USEPA standard whereas 38.6% exceeded the standard after 1980. Based on our data the probability of  $\text{NO}_3^-$  concentrations in recharging groundwater at these sites exceeding 10  $\text{mg L}^{-1}$  has increased from <1% in the 1940s to >50% by 2000 (Figure 5).



**FIGURE 5. Predicted probabilities of  $\text{NO}_3^-$  concentrations in recharging groundwater exceeding 10  $\text{mg L}^{-1}$  as N (red line) in the predominantly agricultural areas examined in this study. Annual fertilizer N use data for the U.S. since 1945 are also shown. Probabilities (percent) in these study areas have increased from <1% in the 1940s to over 50% by 2000.**

The limited denitrification in these aquifers (Figure 4d) points out the potential sensitivity of this groundwater to  $\text{NO}_3^-$  contamination. As this younger groundwater having larger  $\text{NO}_3^-$  concentrations moves deeper into these aquifers, we would expect to see  $\text{NO}_3^-$  concentrations increase. Already China and India have surpassed the U.S. in annual N fertilizer usage at about 32 and 14  $\text{Tg y}^{-1}$ , respectively (22), compared to about 12  $\text{Tg y}^{-1}$  in the U.S. In some aquifers susceptible to contamination  $\text{NO}_3^-$  concentrations have already been reported as high as 67  $\text{mg L}^{-1}$  in China and >400  $\text{mg L}^{-1}$  in India (23, 24). These results suggest that increased application of N and associated increases of  $\text{NO}_3^-$  concentrations in groundwater may be contributing to global health impacts.

The phenomenon of long groundwater residence times also has potential lag effects with respect to surface water quality. Most surficial aquifers are directly connected to a receiving water body. In aerobic aquifers where  $\text{NO}_3^-$  can persist indefinitely, the N stored there may take decades to centuries before it reaches a discharge zone at a receiving water body. Consequently,  $\text{NO}_3^-$  concentrations in many streams represent a mixture of discharging groundwater of varying ages and  $\text{NO}_3^-$  concentrations depending on the residence times of groundwater, the history of N inputs to the aquifer, the denitrification potential of the aquifer, and  $\text{NO}_3^-$  attenuation in riparian and hyporheic zones (25, 26). Streams receiving water from aquifers with short residence times may already be at steady state with respect to their  $\text{NO}_3^-$  concentrations. However, streams fed by aquifers having longer residence times can be expected to display increasing  $\text{NO}_3^-$  concentrations as the fraction of discharging groundwater that predates intensive nitrogen application decreases with time (e.g., refs 26–28). Conversely, where  $\text{NO}_3^-$  inputs are decreased, a lag can be expected in the response in both groundwater and surface water concentrations. The impact of this phenomenon has already been noted for some European rivers where  $\text{NO}_3^-$  concentrations have remained elevated in spite of reductions in  $\text{NO}_3^-$  loadings in their watersheds (29).

### Implications for Climate Change

IPCC results have shown that increases in atmospheric concentrations of global warming gases have been occurring for about 200 y and the resulting global warming is projected to continue for centuries (30). While there is little doubt that global temperatures are increasing, uncertainty remains over the magnitude of these increases. This uncertainty results in part from an incomplete understanding of the sources of

heat-trapping gases as well as the processes involved. N<sub>2</sub>O is one of the four most important of these gases and has a heat trapping capacity about 310 times that of CO<sub>2</sub> (31). Although there are natural sources of N<sub>2</sub>O, anthropogenic emissions are important sources, especially those associated with agriculture. The IPCC methods for estimating the sources and amounts of N<sub>2</sub>O emissions have been criticized for (1) assuming that all N<sub>2</sub>O emissions occur during the same year in which agricultural applications of fertilizer N are applied, (2) overestimating the amount of leaching with the default value of 30%, and (3) overestimating the emission factors for groundwater, streams, and estuaries (7, 10, 30, 31), all of which contribute to uncertainty.

Groundwater is commonly mentioned as an important potential reservoir of N (2, 10) and our data, which show that N applied as much as 60 y ago can still be found in these aquifers, support that assumption. Because gases like N<sub>2</sub>O remain in solution in groundwater until they reach the discharge point and re-equilibrate with the atmosphere (17), this may result in multidecade lags between the time N enters groundwater and its subsequent release in a discharge zone. This time lag currently is not being considered in climate change models (2, 7, 10) in that IPCC methods assume that N<sub>2</sub>O generated by denitrification is released to the atmosphere during the year in which the original N was applied (7, 10). Consequently, the NO<sub>3</sub><sup>-</sup> and N<sub>2</sub>O currently being released from groundwater in many discharge zones may have entered the groundwater system many decades earlier (25), and the NO<sub>3</sub><sup>-</sup> recharging today as well as its reaction products, particularly N<sub>2</sub>O, may not be released for several decades in the future. The net result is that current IPCC inventories of N<sub>2</sub>O emissions from groundwater may be overestimates because N applications were much smaller several decades ago, adding uncertainty to global warming predictions.

In our analysis the equivalent of about 14–18.3% of the N reaching the land surface as fertilizer, animal manure, and atmospheric deposition leached to groundwater. This 14–18.3% leaching rate is significantly less than the IPCC recommended value of 30%, suggesting a potential overestimation of groundwater N<sub>2</sub>O contributions to climate change as has been suggested previously (10, 30, 31). In the U.S. this percentage represents about 2–2.6 Tg N y<sup>-1</sup> and globally about 17–22 Tg N y<sup>-1</sup> (18) indicating that there is a large unaccounted pool of N that has been accumulating in aquifers over the last 60 y. Recent changes to the IPCC methods (9) reduced the N<sub>2</sub>O emission factors considerably but this can still result in emission estimates that exceed measured N<sub>2</sub>O increases. Also, the IPCC retained the 30% leaching rate. Our results indicate that the leaching rate should still be reduced to about 15% potentially cutting N<sub>2</sub>O emission rates in half again. The lags we see in groundwater also suggest that a time lag should be added to the IPCC methods to account for the legacy effect of long residence times of groundwater. These changes would help bring N<sub>2</sub>O emission estimates into closer agreement with measured increases and potentially reduce uncertainty.

Nitrogen in its various forms has become both an essential agricultural nutrient and a major waste product of society during the past 60 years. This N trend is increasing as more nations expand its use to support growing populations and industrial production. The excess amounts of N released can result in groundwater and surface water pollution and contribute to global warming. While high nitrate levels can be a concern on their own, because of long groundwater residence times, steadily declining water quality may result as the fraction of water that predates industrial agriculture decreases with time. The net result is we are creating a N pollution legacy that may affect future generations for decades to come.

Larry J. Puckett recently retired as a research ecologist with the National Water Quality Assessment (NAWQA) Program at the U.S. Geological Survey, and is now located in Asheville, NC. Anthony J. Tesoriero is a research hydrologist with the NAWQA Program at the U.S. Geological Survey in Portland, OR. Neil M. Dubrovsky is a hydrologist and chief of the NAWQA Nutrients and Trace Elements Synthesis Team in Sacramento, CA.

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## Supporting Information Available

More detailed information on the methods and results. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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