

Improving Predictions of Nitrogen Effects on Beneficial Uses of Water

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Chapter E of

Knowledge Gaps and Opportunities for Understanding Water-Quality Processes Affecting Water Availability for Beneficial Uses

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Abbreviations

ANRA	assimilatory nitrate reduction to ammonium
CFC	chlorofluorocarbon
DNRA	dissimilatory nitrate reduction to ammonium
EPA	U.S. Environmental Protection Agency
HAB	harmful algal bloom
IWS	Integrated Water Science
MCL	maximum contaminant level
PWS	public water supplies
SPARROW	SPAtially Referenced Regression On Watershed attribute model
USGS	U.S. Geological Survey
WMA	Water Resources Mission Area

Chemical Symbols

Ar	argon
Ca	calcium
C	carbon
Cl	chlorine
F	fluorine
He	helium
H	hydrogen
Fe	iron
Kr	krypton
Mn	manganese
N	nitrogen
O	oxygen
Na	sodium
S	sulfur

Chapter E

Improving Predictions of Nitrogen Effects on Beneficial Uses of Water

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Purpose and Scope

This chapter is focused on identifying knowledge and data gaps, that if filled, would improve predictions of nitrogen (N) effects on beneficial uses of water resources. The gaps identified in this chapter are not intended to be comprehensive but are instead focused on key opportunities for the U.S. Geological Survey (USGS) Water Resources Mission Area (WMA, <https://www.usgs.gov/mission-areas/water-resources>). Nitrogen effects on ecosystems are not addressed directly in this chapter but are covered in the companion Open-File Report to this publication (Harvey and others, 2024) in their chapter B “Coupled Nutrient-Carbon Cycle Processes and Related Ecological-Flow Drivers.”

Statement of the Problem

Human activities have roughly doubled the amount of reactive N that enters the terrestrial biosphere since industrialization, with crop production by far the largest component of this increase (Smil, 1999). Even sharper increases in reactive N have been observed in developing countries in recent decades (Gu and others, 2015). With no imminently viable alternative to N fixed by the Haber-Bosch process, reactive N is expected to continue to increase in the next several decades to feed a growing population (Smil, 1999; Galloway and others, 2004). While increases in reactive N have been essential to feeding a rapidly growing world population, they have also led to negative environmental effects (Erisman and others, 2013), including degradation of drinking water supplies (Pennino and others, 2020), increasing human health concerns (Ward and others, 2018), nutrient enrichment of aquatic ecosystems (Boesch, 2002; Rabalais, 2002) and contributions to global climate change (Fagodiya and others, 2017; Thompson and others, 2019).

Nitrate is the form of reactive N that poses the greatest threat to beneficial uses, both in the United States and globally; nitrate is among the compounds most likely to exceed U.S. Environmental Protection Agency (EPA) maximum contaminant levels (MCLs) in public water supplies (PWS) (Allaire and others, 2018). Nitrate

concentrations exceeded MCLs in 1.3 percent of catchments containing groundwater or surface water PWS (Pennino and others, 2020). While nitrate MCL exceedances in surface-water supplied PWS are becoming rarer, groundwater-supplied PWS exceedances are increasing (Pennino and others, 2017). Assessments of groundwater sources of private domestic and public drinking water supplies also indicate that nitrate is one of the most common threats to drinking-water quality, with nitrate concentrations in groundwater exceeding the MCL in 4 percent and 2 percent of the private and public drinking water sources, respectively (DeSimone, 2009; Toccalino and others, 2010). The highest risk of an MCL exceedance in a groundwater PWS was found in areas with intensive cropland such as the Central Valley of California, Central Columbia Plateau in Washington, and the Great Plains; MCL exceedances in surface water were more common in the non-mountainous west and the southwest (Pennino and others, 2020). Shallow groundwater beneath agricultural areas poses the greatest risk, with over 20 percent of the wells in this environment exceeding the MCL in a nationwide survey (Burow and others, 2010). The human health effects may be more widespread than indicated by MCL exceedance frequency, as some epidemiological studies have indicated elevated risk of cancers and birth defects with ingestion of nitrate at concentrations below the MCL (Schullehner and others, 2018; Ward and others, 2018; Temkin and others, 2019; Mathewson and others, 2020).

Excess N has also resulted in adverse effects to ecosystems and various beneficial uses of surface water (streams, lakes, estuaries), with more than 40 percent of streams and rivers in the United States in poor condition with respect to nitrogen concentration (EPA, 2016). High total N concentrations are predicted for streams in many agricultural areas in the United States (Bellmore and others, 2018; Shen and others, 2020) and have been linked to many adverse effects, such as hypoxia, harmful and nuisance algal blooms, and species shifts leading to biodiversity loss (Davidson and others, 2011).

Although N concentrations in streams commonly are correlated with N applications to the land surface (Bellmore and others, 2018), such correlations are complicated by highly variable pathways, travel times, and transformations of N during transport from the land surface to streams (fig. E1).

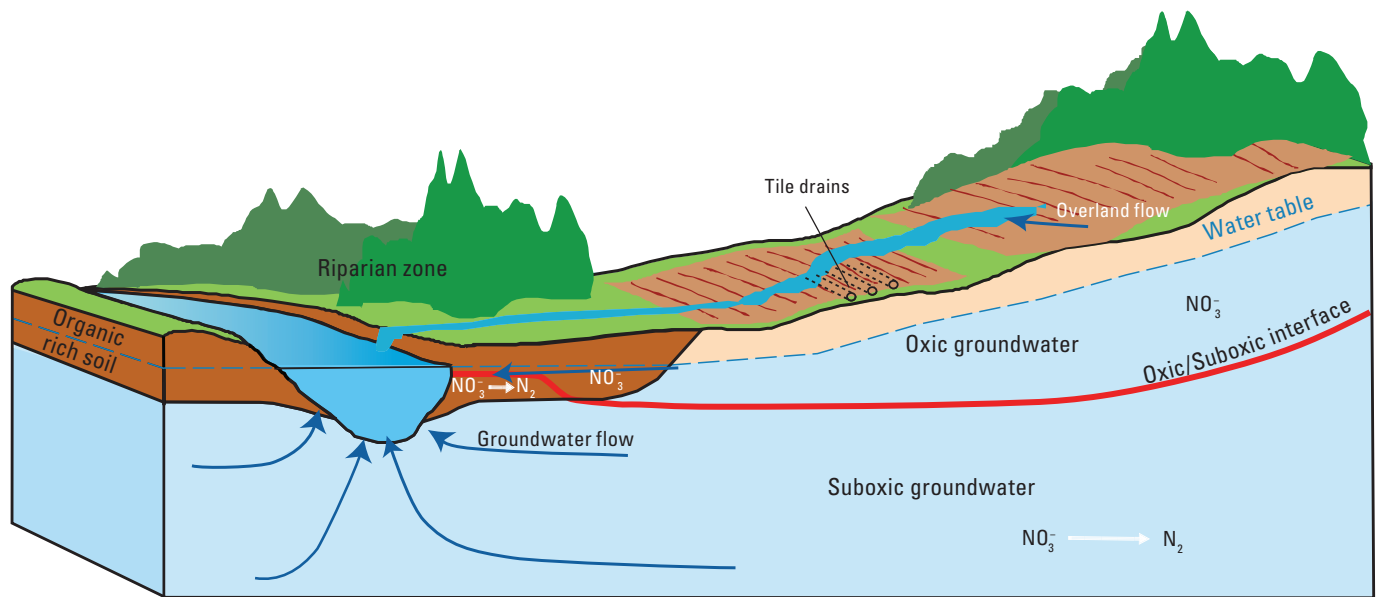


Figure E1. Block diagram showing nitrate (NO₃⁻) transport pathways from the land surface to groundwater and streams and areas of denitrification to nitrogen (N₂). Modified from Wherry and others (2021).

For example, agricultural nitrate can be delivered to streams rapidly and efficiently through surface runoff and tile drains (Tomer and others, 2010), but more slowly and commonly less efficiently (more attenuation) through deeper groundwater flow paths (Sanford and Pope, 2013). Nitrate can be attenuated further after being discharged into streams, rivers, lakes, wetlands, and estuaries (Seitzinger and others, 2006). The combined results of these processes cause much variability in the timing and magnitude of excess nitrate delivery to water supplies and N-sensitive ecosystems.

Other issues related to N transport and transformations include elevated groundwater concentrations of ammonium from landfills, wastewater disposal, and natural production in aquifers (Manning and Hutcheon, 2004; Cozzarelli and others, 2011). Emissions of gaseous forms of N to the atmosphere from soils, wetlands, and surface waters also can be problematic; for example, ammonia gas can be a source of excess N in atmospheric deposition (Tian and others, 2020), and nitrous oxide is a potent greenhouse gas (Pardo and others, 2011; Xu and others, 2019).

Status of Knowledge and Capabilities

Limitations on the beneficial uses of water due to high nitrate concentrations are commonly the result of human activities, especially those associated with agriculture and wastewater disposal (Pennino and others, 2020). Numerous studies have documented that nitrate concentrations in groundwater and streams typically are higher in agricultural areas than in urban or undeveloped settings (Burow and others, 2010; Dubrovsky and others, 2010). Conversely, nitrate concentrations in groundwater and streams in undeveloped settings typically are low and do not

exceed MCLs. Anthropogenic N inputs that can lead to nitrate contamination include fertilizer applications, animal waste infiltration (manure spreading, lagoons), wastewater disposal (including septic systems), enhanced biologic N fixation, and atmospheric deposition (van der Schans and others, 2009; Bellmore and others, 2018). While anthropogenic sources of N have increased dramatically since industrialization (Galloway and others, 2004), natural sources of nitrate also can affect water quality in some areas, especially in arid regions (Walvoord and others, 2003; Jackson and others, 2015; Linhoff and Lunzer, 2021). For example, nitrate concentrations in groundwater may be elevated where natural recharge rates are low and where long-term nitrate accumulations in soils are leached by flooding, irrigation, or artificial recharge. In addition, disturbance and drainage of organic-rich soils can cause enhanced N mineralization and oxidation to nitrate.

Nitrate is highly soluble and mobile in water, but it also can be highly reactive, depending on local conditions. Nitrate is produced biogeochemically by oxidation of reduced N in soils and other oxic environments, abiotically by commercial processes, and by photochemical reactions in the atmosphere. Nitrate is consumed by biologic uptake and microbial reduction to other N species. Denitrification has been suggested as a dominant process causing the loss of nitrate in groundwater (Böhlke and Denver, 1995; Tesoriero and others, 2000; Böhlke, 2002; Seitzinger and others, 2006; Green and others, 2008). Denitrification is inhibited by dissolved oxygen (O₂). As a result, high nitrate concentrations typically are limited to oxic portions of aquifers, and indicators of groundwater redox conditions are often good predictors of denitrification extent (Hinkle and Tesoriero, 2014). While denitrification has long been considered an important process for removing nitrate from groundwater, increasing attention has been given to other pathways such as assimilatory nitrate reduction to ammonium (ANRA), dissimilatory nitrate reduction to ammonium

(DNRA), and anaerobic ammonium oxidation (Henson and others, 2017). Recent studies suggest anaerobic ammonium oxidation (anammox) rates may rival or exceed denitrification in areas where fixed N persists and dissolved O₂ is depleted, such as wetlands and groundwater affected by wastewater (Smith and others, 2015; Li and others, 2021). Other forms of N include organic N compounds, ammonium and (or) ammonia, nitrite, nitrous oxide, and N₂ gas, all of which can be related to sources or sinks for nitrate and may also cause water-quality constraints (for example, ammonia toxicity, nitrous oxide as a greenhouse gas).

Although the major sources of excess N and processes affecting mobility are generally understood, the spatial distribution of elevated N concentrations, the processes that affect its fate and transport, and the timing of water-quality changes in response to changing inputs remain uncertain. Groundwater residence times are highly variable and range from less than a year to many thousands of years (Edmunds and others, 2002), and must be considered in order to accurately predict changes in water quality that result from changes in land use practices (Meals and others, 2010). Spatial and temporal variations in N sources and mobility must be understood and quantified at various scales to support accurate modeling and optimum management strategies. For example, some effects of timing are illustrated in the many studies indicating stable or increasing nitrate concentrations in water-supply wells and streams, despite decreasing N loading to the land surface (Sprague and others, 2011; Eberts and others, 2012; Sanford and Pope, 2013; Van Meter and Basu, 2015, 2017).

Gap Analysis and Approaches

Predictions of N effects on beneficial uses are limited by an inadequate quantitative understanding of N sources, pathways, and timing of N delivery from the landscape to wells and surface waters, and the distribution and effects of N transformations throughout the water cycle. Here, we identify three conceptual gaps (table E1) that represent areas where further scientific understanding and technical ability are needed to monitor and predict water quality related to the N cycle:

1. Nitrogen source identification and tracking,
2. Nitrogen transport pathways and transit times to streams and wells, and
3. Distribution and controls of the natural attenuation of nitrate.

Gap 1. Nitrogen Source Identification and Tracking

Knowledge Gaps

Although the major sources of excess N are generally understood, their distributions and relative effects on water quality locally remain uncertain. Watershed N management is increasingly being optimized by targeting specific areas for implementation of best management practices, which requires

improved spatial and temporal resolution of different source contributions. Evaluating the effectiveness of best management practices also requires predictions of the timing and reactivity of N during transport; these issues are addressed in knowledge gaps 2 and 3. Nitrate concentrations and fluxes in groundwater and surface water depend on N source strengths, aquifer recharge rates, discharge rates, and streamflows on multiple time scales. Improved quantitative understanding of N sources is needed for modeling and mitigation. For example, understanding changes in nitrate sources with changing streamflow may be requisite for managing nonpoint-source N pollution in an era of changing climate (Kaushal and others, 2011). Although temporally intensive monitoring programs provide quantitative information about watershed N yields and trends at selected stream sites, more spatially detailed data are needed to identify local source areas for high-resolution watershed modeling and for locating spatially targeted best management practices. One opportunity to improve our understanding is by relating spatially detailed data with landscape variables describing N sources using machine learning.

Isotopic data commonly are used to assess sources and processes affecting the distributions of nutrients and other contaminants in groundwater and surface water (Hinkle and others, 2007; Kaushal and others, 2011; Nikolenko and others, 2018; Matiatos and others, 2021). While the isotopic composition of N and O in nitrate can be related to its sources and sinks throughout the water cycle, there are important uncertainties in some of the widely held assumptions about how the isotopic data should be interpreted. For example, there is considerable uncertainty in the isotopic fractionation factors for major nitrate transformations, and temporal variation in the isotopic composition of nitrate may confound source identification (Loo and others, 2017; Boshers and others, 2019; Asamoto and others, 2021; Yu and others, 2021). Similar issues apply to other N species such as ammonium/ammonia, nitrous oxide, organic N, and N gas, which must be included with nitrate in models of the physical and biogeochemical cycling of N.

Approaches to Fill Knowledge Gaps

Nitrate Isotopes—Metadata Analysis

A systematic national-scale compilation and evaluation of nitrate isotopic data along with ancillary data from multiple sources could provide new insights and guidance for incorporating isotope data into integrated water availability assessments and watershed water-quality modeling at local, regional, and national scales. One approach would be to compare existing nitrate isotopic data with predictions of nitrate concentrations and controlling factors from machine learning models (for example, Ransom and others, 2021) or with other selected sets of landscape variables. Metadata analyses could include readily available USGS datasets, external datasets, and targeted compilations of results from published local studies. Inclusion of data from selected local studies could help expand the scope of variation in environmental conditions (climate, geology, land use, and so forth) that would be targeted as explanatory variables.

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Table E1. Summary of nitrogen gap analysis for understanding water-quality processes affecting water availability for beneficial uses in the United States.

[N, nitrogen; LPM, lumped parameter model]

Topic	Knowledge Gap	Importance	Proposed Approaches
Nitrogen source identification and tracking	Distribution and relative magnitude of various N sources are not known with sufficient spatial and temporal resolution.	Critical for the assessment, monitoring, and development of nutrient management strategies.	Improve analytical techniques and interpretive models for stable isotopes of nitrate and related constituents. Improve spatial resolution of nitrate data in small streams. Build new statistical models relating concentrations of nitrate and other constituents with sources and other landscape factors.
Nitrogen transport pathways and transit times to wells and surface waters	Transit times of nitrate delivery from the land surface to wells and surface waters are often not known or poorly constrained.	Accurate transit time characterizations have many uses, including predicting and assessing outcomes of management practices, developing nutrient budgets and trends, and estimating degradation rates.	Initiate basin-scale monitoring of tritium in surface water. Develop tritium in recharge and precipitation records. Create and maintain national-scale age-tracer synthesis dataset. Use more tracers with unique age ranges. Identify novel tracers. Incorporate multiple tracers in LPM and distributed parameter models.
Distribution and controls of natural attenuation of nitrate	Nitrate reduction processes and rates are highly variable and difficult to predict.	Critical for accurate prediction of groundwater vulnerability and vulnerability of streams to groundwater sources of N.	Discern reaction processes and rates using field studies, with a focus on surface-water and groundwater interfaces. Increase coordination of research with specific stakeholder actions. Perform large-scale machine-learning studies to delineate zones where nitrate transformations are expected.

Maps, plots, statistics, and machine learning methods (for example, boosted regression, random forest) could be used to relate nitrate isotope data to information about sample chemistry and environmental setting, such as climate, land use, geology, major ions, redox, and the isotopic composition of water. Machine learning modeling results, including variable importance measures and partial dependence plots would be used to identify key sources and transformations affecting nitrate isotope variations. In parallel, selected sample sets representing especially well-characterized, and widely varying, environmental conditions and (or) isotopic compositions could be used to answer specific questions and to assist with machine learning training and refinement.

Stable Isotopes—Improved Analytical Approaches

Past improvements in nitrate isotopic analytical techniques have increased the number of isotope ratios that can be evaluated ($\delta^{15}\text{N}$, followed by $\delta^{18}\text{O}$, followed by $\delta^{17}\text{O}$), decreased the necessary sample sizes (initially micromoles [μmol], now nanomoles [nmol]), and in some cases increased efficiency of sample preparation and analysis. Nonetheless, not all of these parameters are analyzed routinely in USGS programs, and the USGS cost per analysis for nitrate limits the accessibility of such data at regional and national scales. Additional analytical chemistry research to improve isotopic analytical methods (for example, incorporating laser spectroscopic methods or direct measurement of intact molecular species) could potentially reduce costs and turn-around times, while also providing more diverse kinds of isotopic information (Wassenaar and others, 2018; Hilkert

and others, 2021). Co-located isotopic analyses of other redox-sensitive compounds (for example, sulfide, sulfate, organic and inorganic carbon [C], ammonium) could be applied more routinely in studies designed to improve understanding of redox reactions and geologic controls on the distribution of nitrate. Development of such techniques could contribute to more informed applications of isotopic data in N monitoring, assessment, and modeling in aquifers and watersheds. In selected situations, new methods could be applied to archived samples from previous studies, or simultaneously to new samples and to archived samples to document trends that might be related to changing natural or anthropogenic factors. Preservation of sample archives could be a priority for these and many other potentially important applications.

Nitrate Intensive Spatial Surveys

Watershed N model calibrations commonly rely heavily on intensive monitoring data from selected stream sites. Such data provide defensible quantitative values of streamflow and constituent fluxes over time, useful for regional mass balance and long-term trend analyses. However, improvements in understanding and management likely will require more spatially distributed stream monitoring data to capture the effects of variations in land use, geology, and hydrology within a watershed. Because it is expensive to install quantitative monitoring sites at fine spatial resolution, there is a need to expand the acquisition of fine-scale distributed spatial data within stream networks during representative flow conditions (that is, synoptic sampling).

Simultaneously, watershed modeling approaches should be developed for relating these two data dimensions to each other (statistically or functionally), to produce higher resolution estimated datasets over both space and time. In addition, it may be possible to increase spatial resolution of groundwater data for nitrate and related constituents by increased assimilation of existing data, or new sampling and analyses, from domestic wells and other water-supply wells. Such larger estimated spatial-temporal datasets for nitrate, other constituents, and other relevant factors affecting nitrate sources, fate and transport could potentially provide more robust objectives for higher-resolution watershed models of N sources, transformations, and fluxes.

Approaches described above could be implemented selectively at various scales within Integrated Water Science (IWS) basins. For example, sampling could begin soon for isotopic analyses of water, nitrate, and possibly other constituents, in the Illinois River Basin, where complex spatial and temporal patterns of nitrate discharge are related to multiple sources and variable reactivity (Böhlke and others, 2009; Lin and others, 2019). Sampling could be targeted to maximize the value of the data for distinguishing urban, agricultural, and atmospheric nitrate sources, and to resolve groundwater and surface water nitrate attenuation patterns, all of which vary at inter-annual, seasonal, and event-related time scales. Some types of samples (for example, for stable isotopic analyses of water and nitrate) can be preserved and archived for later analysis. Isotopic analyses of archived samples can be done selectively, to maximize cost-effectiveness.

To improve understanding of watershed heterogeneity (to complement temporal records and monitoring stations), fine-scale spatial (synoptic) sampling and analyses could be employed in selected small watersheds within the Illinois River Basin. Detailed synoptic sampling networks should overlap with selected continuous monitoring sites and focus on representative small subwatersheds (for example, USGS watershed hydrologic unit codes HUC10 or HUC12) that are likely to exhibit distinctive patterns of flow and nutrient concentrations related to local land use and other conditions (for example, agricultural versus urban, tile-drained versus naturally well-drained aquifers). Data from small subwatersheds could reveal the diversity of system responses that coalesce into the mixed source and transport signals at larger stream monitoring sites.

Gap 2. Nitrogen Transport Pathways and Transit Times to Streams and Wells

Knowledge Gaps

There is persistent uncertainty in defining the travel times of the various flow paths that deliver nitrate to wells and surface waters (streams, lakes, coastal waters). This has resulted in poor estimates of nitrate concentrations in wells and streams from event to decadal time scales. For example, the age distribution of groundwater discharging to streams is poorly understood and may cause unexpected mismatches between changes in N management on the land surface and changes in N concentrations in streams

(Böhlke, 2002; Sprague and others, 2011; Van Meter and Basu, 2017; Basu and others 2022). This gap in understanding has limited the ability to predict changes in nitrate concentrations in streams that result from changes made to N management practices. The same gap also limits predictions of nitrate concentration trends in water-supply wells, which depend on groundwater age distributions within aquifers, the positions of the wells within the aquifers, and the history of nitrate concentrations in recharge (Eberts and others, 2012; Eberts and others, 2013). Nitrate trends in wells and streams are affected further by the distribution of nitrate reduction along groundwater and surface-water flow paths, as discussed in the section knowledge gap 3, “Distribution and Controls of Natural Attenuation of Nitrate” of this chapter.

Hydrograph separation and watershed models such as SPARROW (SPATIally Referenced Regression On Watershed attribute, <https://www.usgs.gov/mission-areas/water-resources/science/everything-you-need-know-about-sparrow>) have estimated the pathways and sources of N inputs to streams (Alexander and others, 2008; Miller and others, 2017; Husic and others, 2019). Increases in the amount of high-frequency nutrient monitoring data have expanded the use of these techniques. Estimating lag times between when nutrients are applied to the land surface and when nutrient effects are fully observed in streams has been more challenging and addressed with several modeling approaches (Vero and others, 2018). A seasonally dynamic version of SPARROW has recently been developed that includes time-varying storage effects (Schmadel and others, 2021).

Groundwater dating with chemical and isotopic environmental tracers can provide important information about aquifer recharge and sustainability, and the progress of contaminants in the subsurface; however, improvements are needed, especially for applications to groundwater discharge to wells and surface water bodies such as streams, lakes, and estuaries. Because of mixing from dispersion in the aquifer or from pumping into long screened wells, samples from wells contain mixtures of groundwater with many different ages. Age mixtures may be especially complex in surface waters receiving groundwater discharge because groundwater, soil water, and runoff can contribute varying proportions to the total discharge, each with its own mixed age distribution, and those mixtures can change on various time scales in response to changing hydrologic conditions in the watershed. Tracer measurements in surface waters will reflect those complex mixtures and, in addition, some tracers will be affected by gas-exchange with the atmosphere.

Vadose zone transit times are another major gap, as most groundwater age tracers only account for travel time since a water sample has been isolated from the atmosphere (that is, time of recharge to the aquifer). In fact, vadose zone storage can be a substantial source of nitrate globally (Ascott and others, 2017), with travel times through the vadose zone comprising a significant portion of the overall travel time in some cases (Green and others, 2018). Vadose zone time lags may be decades or longer (McMahon and others, 2006; Fenton and others, 2011; Wang and others, 2012; Wang and others, 2013), requiring their consideration for accurate prediction and assessment of nutrient best management practices (Ascott and others, 2021). Comprehensive evaluation of N storage and release trends also should include

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masses and residence times of soil organic N, which contribute to nitrate runoff and infiltration over a range of time scales (Sebilo and others, 2013; Van Meter and others, 2016).

The majority of the work done to develop constituent transit times with tracers has focused on relatively local landscape and aquifer settings, and there are limited resources for integrating tracer data on a larger scale (Michel and others, 2018; Green and others, 2021). Compilations of tracer concentrations and associated site and project metadata, interpretive values, and citations are not readily available (either for the United States or on a global scale). As a result, synoptic assessments must start from scratch and often must make assumptions about the validity of input data, hydrogeologic setting, and other parameters. Approaches for interpreting tracer data on a synoptic scale are poorly developed and there is need for further research and data for developing multi-aquifer, regional and national scale investigations (McMahon and others, 2011; Visser and others, 2016; Lindsey and others, 2019; Zell and Sanford, 2020). Additionally, there are few examples of national groundwater transport and chemistry models that use tracer data, and considerable further development is needed to obtain national-scale modeling ability that captures the tracer results at a given site.

Approaches to Fill Knowledge Gaps

The time that water spends traveling in the subsurface is fundamental to understanding a watershed's response to changes at the land surface (for example, anthropogenic inputs). The distribution of transit times in a watershed describes how water and solutes are retained and released, which in turn affects biogeochemical cycling and contaminant persistence (McGuire and McDonnell, 2006; Sprenger and others, 2019). Several approaches are suggested that will improve assessments of the timing and delivery of nitrate to wells and streams.

Multi-Tracer Studies in Integrated Water Science Basins

The IWS basins provide excellent opportunities to address this important issue. Specifically, supplementing the existing sampling strategy to include environmental tracers at multiple scales could advance our understanding of transit times and provide valuable calibration targets for models. For example, transit time distributions in groundwater discharge could be compared to time lags estimated by seasonally dynamic SPARROW watershed models and may help quantify travel times of pathways defined by hydrograph separation models. Hydrograph separation models often define a slow flow component but are typically not able to quantify the travel time for this component (Miller and others, 2017). Transit time distributions may be useful for evaluating delayed responses to best management practices designed to reduce N loads to streams, as well as for identifying seasonal and climate related variations in nitrate sources and loads. Proposed analytes would include tritium (^3H), stable isotopes of water, dissolved gases, and various other chemical constituents. Tracer measurements in surface waters will reflect the complex mixtures of the many flow paths that deliver

water and solutes to a stream, as well as potential modifications within a stream corridor. In general, such complexities require simultaneous measurements of multiple tracers with contrasting input signals, combined with hydrogeologic insight and mathematical formulations to evaluate the age distributions.

Dissolved gases, tritium, stable isotopes of water and other chemical constituents have been used to determine groundwater transit times through catchments from recharge to discharge. For example, combined analyses of major dissolved gases and environmental gas tracers in streams can be used to estimate mean groundwater transit times through catchments during base flow conditions where streams undergo large diurnal temperature shifts and where relative rates of groundwater discharge and air-water exchange are favorable (Sanford and others, 2015). The recent stabilization of the tritium deposition rate presents the opportunity to establish the mean age of base flow in streams with a small number of samples (Morgenstern and others, 2010; Stewart and Morgenstern, 2016). For example, collection of tritium samples at intervals of 2 to 3 years may allow for the effective discrimination between different possible age solutions (Gallart and others, 2016). Recently, it has been demonstrated that tritium and stable hydrogen (H) and O isotopes of stream water can be used to constrain varying groundwater residence times contributing to streamflow over a range of flow conditions (Cartwright and others, 2020; Rodriguez and others, 2021). Concentrations of major ions and other constituents may also provide important information on transit times of stream base flow where steady rates of chemical weathering of aquifer material occur. Correlations between sodium (Na), calcium (Ca) and silica (SiO_2) and groundwater age have been used to estimate the mean residence time of base flow (Burns and others, 2003) and groundwater (Tesoriero and others, 2005). Fluoride (F^-) and chloride (Cl^-) were among the most important variables for predicting groundwater age in a recent study (Green and others, 2021) and may also hold promise for estimating residence times of groundwater contributing to streams. Vadose zone transit times should also be assessed using process-based unsaturated zone modeling techniques with suitable tracer data for calibration; these results can be combined with groundwater transport modeling results to estimate overall lag times (Wang and others, 2013; Green and others, 2018).

Geophysical approaches can add additional information to transit time assessments by providing details of aquifer structure, density, and locations of discharge into surface water (Lane and others, 2016). These approaches are powerful when combined with age-tracer related information for relating the spatial occurrence of nitrate discharge areas with mean transit time and (or) transit time distributions of the discharge. Data and interpretive models for multiple tracers generally will be needed to resolve age distributions in mixtures of younger and older water, which may or may not have simple or smooth functions (Green and others, 2010; Jurgens and others, 2012; Green and others, 2014; Green and others, 2016; Sprenger and others, 2019). This is particularly true in heterogeneous aquifers and many groundwater discharge areas, especially where seasonal and event-related

variations in flow and nitrate concentration need to be addressed (Rinaldo and others, 2015).

Development and Increased Use of Additional Tracers

Transit times of nitrate in groundwater are often determined using groundwater age tracers. Atmospheric tracers capable of determining the age of young water (less than 100 years), such as chlorofluorocarbons (CFCs), tritium-helium ($^3\text{H-He}$) and sulfur hexafluoride (SF_6), have been especially useful for estimating transit times, as some of the major changes in anthropogenic N loading have overlapped the period spanned by the atmospheric histories of these tracers (Böhlke and Denver, 1995; Böhlke, 2002; Puckett and others, 2011). This approach remains powerful, and there are likely further opportunities to refine and extend groundwater transit time determinations as additional age tracers become available. Recent advances in noble gas radioisotope sampling and detection methods have made sampling for krypton-85 (^{85}Kr), argon-39 (^{39}Ar), and ^{81}Kr more accessible (Aeschbach-Hertig, 2014; Lu and others, 2014). These tracers can resolve ages ranging from modern to millions of years. Argon-39 can be used for dating water between 70 and 1,000 yrs old, while both ^{39}Ar and ^{81}Kr can help refine dates from carbon-14 (^{14}C) dating when carbonate systems deviate from equilibrium (Seltzer and others, 2021). Krypton-85 is valuable for resolving decade-scale transit times for groundwater with reducing conditions, which is crucial as these conditions can transform CFC tracers, rendering them useless (Gröning and others, 2006). There are other modern tracer candidates such as perfluorocarbons (CF_4 , C_2F_6 , C_4F_8 , and others), minor CFCs (CFC-13, CFC-114, CFC-115, and others) and halons (H-1211, H-1301) that may also be used to determine nitrate transit times in groundwater, providing more accuracy and mixing information than the current suite of age tracers (Beyer and others, 2014; Haase and Busenberg, 2014; Bartyzel and Rozanski, 2016; Beyer and others, 2017).

Some new possibilities may exist to date groundwater by measuring abundances of artificial chemicals or chemical structures that have been manufactured and applied on the landscape over time. For example, a change in the chiral form of a manufactured pesticide is being investigated as an indicator of the age distribution of groundwater discharge to streams in agricultural areas with high nitrate loads (Rice and others, 2016). In principle, such tracers could be combined with other tracers with different input histories to resolve various types of age-distribution models in groundwater and surface water (Jurgens and others, 2012; Rinaldo and others, 2015).

Improving the Understanding of Tritium Deposition and Recharge

Refinements in our understanding of tritium deposition rates and recharge mechanisms could result in increased accuracy of all tritium-based approaches. Currently the best understanding of tritium deposition is a gridded approach based on data collected mostly in the 1970s and 1980s. The current model of the tritium input function (Michel and others, 2018) could be refined by

adding recently collected data and by establishing a modern precipitation monitoring program. Notably, seasonal variability of tritium in precipitation, recharge, and discharge is not constrained with high precision, and contributions of non-atmospheric tritium to groundwater discharge (for example, from landfills and other sources) are not well documented. Extrapolation methods used to establish the tritium input function lose accuracy if seasonal and temporal trends in tritium are not captured; this loss in accuracy then propagates to other empirical and interpreted values such as recharge rates and transit times (Li and Si, 2008). Additionally, by studying tritium deposition and recharge, the fundamental atmospheric processes that govern tritium creation might be better understood, with the ultimate goal that they could be modeled directly (Tadros and others, 2014; Palcsu and others, 2018).

Gap 3. Distribution and Controls of Natural Attenuation of Nitrate

Knowledge Gaps

The rates and dominant pathways of nitrate reduction have been determined at the field scale but are rarely understood at regional or larger scales. Denitrification is a well-studied process but its occurrence in groundwater is dependent on redox gradients that are not well defined spatially. Redox gradients in groundwater can have a significant effect on both the fate and lag times of nitrate transported from the landscape to groundwater and streams (Tesoriero and others, 2021). While recent advances using machine learning and statistical techniques have improved predictions of redox conditions in aquifers (Tesoriero and others, 2015, 2017; Close and others, 2016; Knoll and others, 2020), regional and larger scale redox assessments have often been compromised by limited information on geology, mineralogy, and geochemistry over a range of depths and spatial scales in the subsurface (Koch and others, 2019). In addition, the distribution and relative importance of other nitrate reduction processes (for example, anammox, DNRA, ANRA) that affect watershed N mass balance modeling are not known.

Nitrate reduction rates and pathways near groundwater discharge sites are likely to be spatially and temporally more complex than those in upgradient regions within aquifers, requiring more detailed parameterizations of near-stream hydrogeology and biogeochemistry. For example, agricultural or septic-system nitrate transmitted through surficial aquifers in oxic groundwater may encounter reducing conditions locally in riparian lowlands near streams (Hill, 2018), or complex and variable flow and mixing relations with reduced saline groundwater near coastal shorelines (Santos and others, 2021). Further reactions occur after groundwater discharges into surface water, where nitrate production and loss result from biologic activity in the water column, benthos, or hyporheic zone. As a result, net nitrate removal efficiencies and discharge fluxes between groundwater and surface

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water interfaces have large uncertainties. Resolving these complexities and scaling their results for watershed models are persistent problems requiring multiple approaches.

Approaches to Fill Knowledge Gaps

Multi-Disciplinary Studies in Integrated Water Science Basins

Multi-disciplinary targeted field studies could determine nitrate reduction rates and pathways and provide a comprehensive evaluation of sources, transport, and transformation. Focus should be placed on the spatial and temporal variability and factors controlling nitrate reduction rates and pathways in groundwater discharge areas and other areas where variable fluxes and sharp redox gradients are expected. Comprehensive investigations should include detailed characterizations of the hydrogeology and biogeochemistry of watersheds, calling on the multi-tracer transit time approaches discussed above and (or) coordinating with larger collocated tracer studies as appropriate. Analyses could include groundwater dating, isotopes, microbial communities and activities, geophysics, continuous sensing of physical and chemical parameters, and intensive monitoring of harmful algal blooms (HABs). Such studies would be particularly useful for documenting effects of deliberate human actions such as land use change, best management practices, drainage, irrigation, fertigation, and water re-use. Suitable study sites could be selected based on nitrate risk assessments for both groundwater (for example, machine learning models) and surface water (for example, SPARROW) developed using existing data. Data from synoptic surveys of N loads using mobile sensors could also support site selection. Studies to document changes related to specific human activities would need to be coordinated with stakeholders and other Federal, State, and local agencies, and they would need to be relatively long-term (pre- and post-change), iterative, and with modeling built in. Ideally, study sites and approaches could be selected to maximize the scientific return from existing stakeholder investments in a basin.

Predicting Redox Conditions and Nitrate Inputs to Streams Using Machine Learning

Machine learning methods could be used to relate explanatory variables to measured concentrations of redox-sensitive constituents and predict redox conditions across the Nation. Multiple redox-sensitive constituents (for example, dissolved O₂, iron [Fe], manganese [Mn]) would be modeled. Explanatory variables could include those describing hydrology, soil chemistry, geology, and land use. Developing a three-dimensional (3-D) framework of subsurface geology, reactivity, and geochemistry from existing data could improve predictions of redox conditions in groundwater and identify data gaps that are limiting the accuracy of these predictions. For example, it will be important to understand the distribution and reactivity of electron donor phases that promote O₂ and nitrate reduction. Model predictions could be generated from regional to national scales. Temporal changes in redox interfaces could be evaluated where redox-sensitive species data are available over multidecadal time

periods and in other areas using vertical flux modeling (Liao and others, 2012). Machine learning predictions of redox conditions in groundwater could be used to delineate nitrate reduction zones for process-based models or used as an explanatory variable for statistical or machine learning models that predict base flow nitrate concentrations in streams (Wherry and others, 2021).

Expected Outcomes

A meta-analysis of nitrate isotope data could provide a much-needed framework for identifying nitrate sources and transformation both for WMA studies as well as those in the broader scientific and water resource communities. A large data set of nitrate isotope and ancillary data could provide an unprecedented opportunity to characterize factors that lead to changes in nitrate isotope ratios. Improved techniques and wider application for isotopic analyses of other N species such as ammonium and N gas, as well as other related redox-sensitive constituents, also could permit more integrated studies of nitrogen transport and transformations.

Improved multiple tracer-based transit time information for vadose zones and saturated zones could enable better predictions of water-quality conditions and trends in groundwater and surface water, particularly in relation to recent changes in nutrient management practices. Much of the current understanding of nutrient loading to surface water is based on statistical regression of flow-concentration relationships and does not readily yield an understanding of the nutrient reservoirs. Tracer-based transit times could provide information that is crucial for determining functional relationships between climate conditions, nutrient input, hydrology, and water quality. Residence times can be used to develop and validate models of nutrient transport, transformation, and loss, resulting in actionable information that indicates where large reservoirs and long flow paths of nutrients exist and provides insight into how changing nutrient application on the landscape will propagate in hydrologic systems.

Multidisciplinary studies in intensively monitored watersheds could produce needed information for evaluating nutrient management strategies, particularly when natural attenuation assessments are coupled with the transit time work. Synoptic studies of N transformations at IWS basins could provide detailed information on how N pathways to groundwater and streams vary as a function of hydrology (including stream order), geology and land use. This information could improve both statistical and process-based modeling predictions of N loading. Identifying nitrate transit times requires identifying the pathways that contain nitrate through an assessment of natural attenuation and identifying the transit times of these pathways using tracers and (or) modeling. Specifically, identifying reaction rates and transit times could inform modeling efforts in the intensively studied basins by identifying the lag times of nitrate pathways through non-reactive zones. Identifying nitrate reduction zones will aid nutrient management strategies; strategies that route water and solutes through these nitrate reduction zones will yield better results.

To scale these findings up, machine learning models could produce 3-D national- and regional-scale estimates of redox conditions in groundwater. These models could predict the depth below the water table at which a redox interface would be encountered and could provide insight on the temporal migration of these interfaces. These interfaces could delineate where redox transformations would be expected, important input for both process-based and statistical water-quality models. These interfaces will be useful both for predicting groundwater susceptibility to nitrate and nitrate concentrations in base flow.

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