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Context is everything: Interacting inputs and landscape characteristics control stream nitrogen

Jiajia Lin[1,2,*], **Jana E. Compton**[1], **Ryan A. Hill**[1], **Alan Herlihy**[1,3], **Robert D. Sabo**[4], **J. Renée Brooks**[1], **Marc Weber**[1], **Brian Pickard**[5], **Steve Paulsen**[1], **John L. Stoddard**[1]

[1]US EPA, Office of Research and Development, Center for Public Health and Environmental Assessment, Pacific Ecological Systems Division, Corvallis, OR 97333

[2]Oak Ridge Institute for Science and Education, Corvallis, OR 97333

[3]Oregon State University, Department of Fisheries and Wildlife, Corvallis, OR 97333

[4]US EPA, Office of Research and Development, Center for Public Health and Environmental Assessment, HEEAD, Washington, DC 20004

[5]Tetra Tech, Inc, Durham, NC 27709

Abstract

To understand the environmental and anthropogenic drivers of stream nitrogen (N) concentrations across the conterminous US, we combined summer low flow data from 4997 streams with watershed information across three survey periods (2000-2014) of the US EPA's National Rivers and Streams Assessment. Watershed N inputs explained 51% of the variation in log transformed stream total N (TN) concentrations. Both N source and input rates influenced stream NO_3/TN ratios and N concentrations. Streams dominated by oxidized N forms (NO_3/TN ratio > 0.50) were more strongly responsive to N input rate compared to streams dominated by other N forms. NO_3 proportional contribution increased with N inputs, supporting N saturation enhanced NO_3 export to aquatic ecosystems. By combining information about N inputs with climatic and landscape factors, random forest models of stream N concentrations explained 70%, 58%, and 60% of the spatial variation in stream concentrations of TN, dissolved inorganic N, and total organic N, respectively. The strength and direction of relationships between watershed drivers and stream N concentrations and forms varied by N input intensity. Model results for high N input watersheds indicated potential contributions from contaminated groundwater to high stream N concentrations, but also the mitigating role of wetlands.

Graphical abstract

*Corresponding author. Address: USEPA, 200 SW 35TH Street, Corvallis, OR 97333. Jlin42@Outlook.com.

Supporting Information

R code for random forest modeling. Text describing study methods and materials. Tables of predictor variables for random forest models and N inventory. Maps of survey sites and ecoregions, and survey results of stream N. Figures demonstrating relationships of stream TN concentration with N input rate at different input level. Figures of results from random forest modeling.

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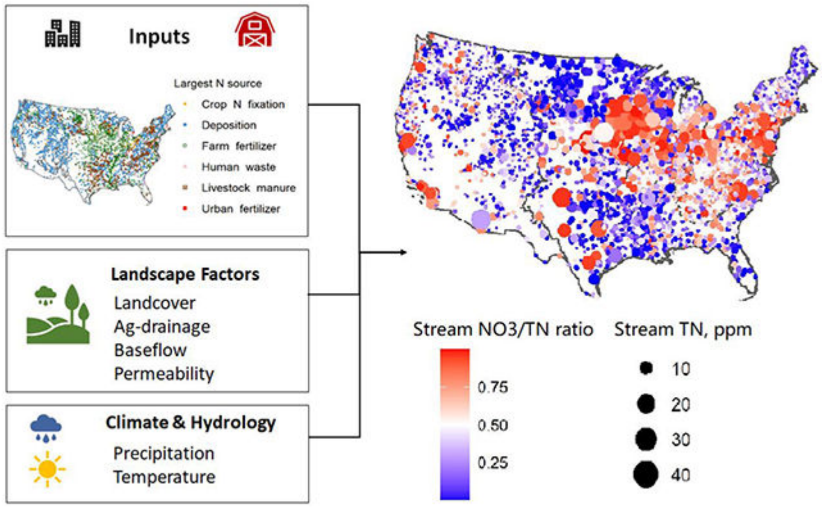

Keywords

N inventory; N concentration; N species; water quality; nutrient; conterminous US; spatial variation; random forest; machine learning

Introduction

Human demand for food, fiber, and energy has reshaped the global nitrogen (N) cycle, leading to an approximate five-fold increase in anthropogenic production of reactive N during the last century, causing a cascade of consequences[1–3]. Excess N input to the landscape can contaminate drinking water supplies[4,5], stimulate the production of greenhouse gas and stratospheric ozone depleting nitrous oxide[6,7] and accelerate eutrophication[8–10].

Understanding the controls on nutrient concentrations is important for managing aquatic ecosystems[17–20]. States often develop criteria for nutrient concentrations to help mitigate and manage the negative outcomes caused by excess nutrients in streams[18,21]. Summer N concentrations are particularly important to track in light of recent evidence that N plays a role in cyanobacterial blooms and toxin formation[22–24] and the documented increase in harmful algal blooms[25]. Despite the importance of nutrient concentration for management, much of the focus of previous work has been on understanding the major driver of river loads for watersheds across the US[26]. To complement the historic efforts predicting N loads, our work focuses on the biologically important summer N concentrations of rivers and streams across the US.

Compilation of spatial datasets of nutrient inputs to watersheds has proven instrumental in modeling stream and river loads[26–29]. Several recent studies examined temporal trends in stream and river N concentrations[30–32], but they did not make direct connections between concentrations and N input rates. Other efforts have focused on a limited set of intensively monitored sites, mainly large streams and rivers, that may not adequately characterize the widespread variability of watershed responses to nutrient inputs[26,33]. More studies are

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needed to connect variation in concentrations to changes in N inventories at large scales. Newly assembled nutrient input inventories [34,35] allow for more direct connections between the variations in N inputs and aquatic N concentrations. Coupled analysis of nutrient inputs and stream N concentrations across many watersheds can aid in assessing water quality issues in rivers and streams at regional or national scales.

In this work, we studied nearly 5000 US watersheds capturing the wide variability in stream N concentrations and the associated watershed characteristics across the country. National nutrient input inventories[34] (NNI) and watershed landscape and climate variables were paired with stream N concentration data from EPA's National Rivers and Stream Assessment (NRSA) to 1) understand whether and to what extent changes in N inputs are reflected in stream concentrations of total N (TN) and N species in the conterminous US (CONUS); 2) understand the relationships between various landscape and climate drivers and stream nutrient levels; and 3) identify the context dependency of these relationships in response to intensifying amounts of N inputs.

Materials and Methods

National Rivers and Streams Assessment (NRSA)

Water chemistry data (concentrations of TN, NO_3, NH_4, and total organic N) originated from the EPA NRSA surveys that have been conducted across the CONUS since 2000 (Figure S1). The first survey cycle was conducted in 2000-2004[36] (Survey 1, n = 1170). Subsequent survey cycles in 2008-2009 (Survey 2, n = 1877) and 2013-2014 (Survey 3, n = 2046).

Across the three surveys, almost all samples were collected during the May-October index period with the goal of indexing summer baseflow conditions. Less than 1% of samples were sampled outside the index period. We present data on NO_3 (NO_3 plus NO_2), NH_4, and TN determined by persulfate digest. We also calculate total organic N (TON) as TN minus NO_3-N and NH_4-N. Further information on field and laboratory protocols can be found in Supporting Information (SI). Roughly 10% of the sites were sampled a second time within the summer index period within each survey year to assess temporal variability relative to spatial variability. Bellmore et al.[38] showed that 80-90% of the variation in NRSA N samples was associated with spatial variation rather than within year variation. In this study, we only used data from the first site visit in our analyses. We combined the data from all three survey cycles into one sample population and conducted analyses of the combined data, to allow focus on the drivers of spatial patterns in N concentrations. Sites were spatially grouped into three ecoregions[39] for our analyses (Figure S1): Western Mountains (also referred to as the West in the study), Plains and Lowlands (also referred to as the Midwest or plains), and Eastern Highlands (also referred to as the East).

We calculated ratios of different N species to TN across sites to explore the spatial distribution and factors influencing watershed N retention and stream chemistry. We categorized NRSA sites based on stream NO_3/TN ratio: the 'oxidized' stream N group with NO_3/TN ratio > 0.50, and the 'reduced' stream N group with NO_3/TN ratio < 0.50. We also separated watersheds into three groups based on N input levels: low input watersheds (n

= 2219) with N input rate <15 kg N ha^{-1}; medium input watersheds (n = 1565) with N input rate ranges between 15 and 50 kg N ha^{-1}; and high input watersheds (n = 1213) with N input rate > 50 kg N ha^{-1}.

Watershed and Climate variables

To model NRSA stream TN concentrations, we used a suite of landscape, climate, and nutrient input data as independent covariates. The landscape data for each NRSA site came from the EPA StreamCat dataset, which contains a wide variety of watershed metrics that are derived from coverages that characterize both natural and anthropogenic landscape features (see SI and Table S1)[40]. From StreamCat, we selected a set of watershed features that we hypothesized would influence stream TN concentrations based on our understanding of such factors and previous research[38], such as land use present in the watershed of each NRSA site (see SI for more details and Table S1 for other variables).

In addition to StreamCat data, we also summarized annual and monthly mean climate variables from PRISM and NASA Earth Observatory data for each watershed from the corresponding year and month when each site was sampled (Table S1). These data included annual and monthly means of precipitation, snow cover, numbers of fires, land surface temperature, and vegetation cover within the watershed. More details on data sources and methods can be found in the SI.

National Nutrient Input Inventory (NNI)

The NNI (downscaled from Sabo et al.[34]) compiles data for many nitrogen sources for the entire CONUS including agricultural and residential fertilizer, crop biological N fixation, land applied manure, human waste, and deposition. We connected each NRSA survey with its closest year of record; Survey 1—NNI 2002; Survey 2—NNI 2007; and Survey 3—NNI 2012. Input NNI rasters were summarized to the NRSA watershed scale using zonal statistical procedures in GIS software (see details in the SI). Total watershed N inputs were calculated by summing agricultural N fertilizer, N-fixing crop cultivation, livestock N waste, urban N fertilizer, human N waste, and total N deposition inputs. Watersheds were categorized based on the proportionally largest N sources described above. These categories were then used in subsequent analyses as shown in the next section.

Spatial and statistical comparisons

We mapped NRSA sample sites by their largest N source to explore spatial patterns of N inputs and sources. In addition, we used linear regression to initially test the relationships between N inputs and stream N concentration. To further investigate regional variations in both N inputs and stream N concentrations, we calculated means and standard errors of response variables (N inputs and stream N concentrations and ratios) at both regional and national levels.

ANOVA and t-test were used to examine the response of stream TN concentration to N input rate and its dependence on stream N type (‘oxidized’ where NO_3/TN > 0.5 vs ‘reduced’) and input level, respectively. We also applied ANOVA to compare stream NO_3/TN ratios for different N input sources and levels to further understand how stream dominant N speciation

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changed with land use and input intensity. These tests were also carried out to examine regional differences in N species.

Random forest models

We used random forest[41] modeling to explore relationships between stream N and watershed features, climate, and N inventories by combining data from the three surveys. Random forest models are robust to violations of the assumptions made by parametric statistical approaches including multicollinearity among predictors[41]. However, to improve model interpretation, we minimized collinearity of predictors by pre-selecting a subset of variables before modeling (see details and code in SI). The final set of 21 predictor variables included 15 variables from StreamCat, PRISM and the Earth Observatory Network, and 6 N input rate variables of six sources from the N inventories (Table S1). With these data, we developed a series of random forest models to explain stream TN and different N species. We combined NO_3 and NH_4 as dissolved inorganic nitrogen (DIN) in our models to avoid potential data and modeling issues caused by too many low values (< detection limit) of NH_4 concentration. There were 4997 data points used in our final analyses after removing erroneous outliers that had TN input rate > 1000 kg N ha^{-1} and/or negative TON values.

The first set of models contained data from the full set of sample sites to explain concentrations of stream TN, DIN, and TON. To examine how the importance and behavior of explanatory variables varied among N input levels, sites were separated into three groups in subsequent N models based on the three N input levels we defined above[42]. Although not required by random forest, stream concentration and N inventories data were natural log transformed to improve interpretations when plotting modeled relationships[43]. We added a ‘1’ to the inventory variables so that zero values could be transformed. The dataset for each model was randomly divided into training (75% of total available data) and testing (25%) datasets to evaluate model performance.

All data analyses were conducted using R programming language[44] (version 3.6.2) and the associated packages (dplyr_0.8.4; randomForest_4.6-14; caret_6.0-86).

Results

Connecting the N inventory to stream N

Sources and rates of N inputs were strongly related to stream N concentrations across the CONUS (Figure 1 & S2). Watersheds where agricultural inputs (farm fertilizer, manure, and crop N fixation) were the major N source, had higher total watershed N input rates and stream TN concentrations. Sites with atmospheric N deposition as the largest watershed N source were associated with lower N input rates and stream TN concentrations. At the national scale, stream TN concentrations were strongly correlated with N input (Figure 1a; r^2 = 0.51, p<=0.001).

Nitrogen source also affected stream N forms. We separated the watersheds into three types based on largest N source: agricultural, deposition and human. On average, sites dominated by agricultural N inputs had significantly higher N concentrations and NO_3/TN ratios than sites where deposition was the largest N source (ANOVA, $p < 0.0001$), but the latter had

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higher proportional TON contributions than agricultural and human types of watersheds (ANOVA, $p < 0.0001$). Watersheds with human waste and urban fertilizer as the largest N source, categorized as the 'human' group, only accounted for about 3.6% of total sampled sites. These sites on average had the highest NO_3/TN ratio and the lowest TON/TN among three land use types (ANOVA, $p < 0.0001$). Within each watershed group where either agricultural inputs or atmospheric deposition was the largest N source, stream NO_3/TN ratio increased significantly with increasing input level (Figure 2a & Table 1a). Within the 'human' group, NO_3/TN ratio changes were either not significant or not computable due to small number of sites (Table 1a). Combining all input groups, the mean NO_3/TN ratios in the low N input, medium N input, and high N input groups were respectively 0.24, 0.37, and 0.51, and mean TON/TN ratios in these watershed groups were 0.71, 0.59, and 0.45, respectively.

The dominant N forms in streams interacted with input rates. Streams where NO_3 was the largest N form, (the 'oxidized' type), exhibited a stronger and steeper relationship with N inputs as compared to the 'reduced' type of streams (Figure 2b). The difference in regression slopes of the two types of watersheds (equal to 0.27) was statistically significant ($p <$ 0.0001). We further examined such difference in slopes at three input levels, and determined that the contrast between 'oxidized' and 'reduced' slopes were minimum and insignificant among low N input watersheds, but grew greater and significant as input level increased (Figure S3).

The three ecoregions (see regions map in Figure S1) varied in N input and stream N chemistry (Table 1b). Western Mountains region, where a large portion of watersheds had deposition as the largest N source, also had the lowest N input rates on average, stream N concentrations, and NO_3/TN ratios compared to the other two regions ($p <$ 0.0001). In contrast, watersheds in the Plains and Lowlands region had the highest mean inputs and stream N concentrations, the latter was enhanced by both high stream NO_3 and TON concentrations. Streams in Eastern Highlands had the highest regional NO_3/TN ratios compared to the other two regions. The 'reduced' type of watersheds had about equal numbers with the 'oxidized' type in the sampled streams in the East, but were more prevalent in the western and plains regions (Table 1b), with streams in the plains showing the highest mean TON and NH_4 concentrations especially in its 'reduced' type. At the regional level, most 'oxidized' type of sites had significantly greater mean N input rate (ANOVA, $p < 0.0001$ except in the Western Mountains) and stream TN concentration (ANOVA, all $p < 0.01$) than those of the 'reduced' type of sites within the same region. (Table 1b).

Random forest models of stream N concentrations

The models that included all sample sites explained 70%, 58%, and 60% of the variation in stream TN, DIN, and TON concentrations, respectively (Figure 3a–3c). Cross validations using the withheld testing dataset yielded r^2 values of 0.90, 0.86, and 0.88, respectively, for TN, DIN, and TON concentrations. The most important predictors varied by N form, indicating that drivers affected cycling of N species in different ways. Agricultural land use and input rates were among the most important variables for all three models. Proportional

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baseflow contribution and the annual mean Normalized Vegetation Difference Index (NDVI) – a standard remotely sensed index of plant greenness and health and generally positive correlated with net primary productivity — were also important across models. Human waste and atmospheric deposition input rates were key to predicting DIN concentrations, while wetland coverage and annual mean precipitation were more critical for the TON model. Annual mean temperature was only important in predicting TON. Agricultural input rates ranked higher than land use percentages in their importance in predicting TN and DIN concentrations.

Subsequent random forest models and partial dependance plots conducted on data subsetted by input level further revealed how different factors influenced stream N species under each N input level (Figure S4–S6). The lowest input category primarily represented watersheds where deposition was the largest source. The highest input category represented a large proportion of sites where fertilizer was the largest source, and the intermediate category had a mixture of largest source types.

For low N input watersheds, vegetation index and baseflow contribution were important predictors and exhibited negative relationships with TON and DIN concentrations (Figure S4). Other than agriculture related variables, wetland coverage also had a positive relationship with stream TON concentration, which was its second most important predictor. N deposition rate and monthly mean precipitation exhibited positive relationships with DIN concentration. Monthly mean areal fire counts (per 1000 km^2 per day) were positively associated with TON, DIN, and TN concentrations when count was > 1. Variable importance and correlations with TN concentration mostly followed those in the TON sub-model (Figure 3d & S4), as a result of TON being a more important contributor to stream N in low N input watersheds.

For watersheds with intermediate N input level, predictors associated with direct human activities became important in DIN and TN sub-models, such as urban land use (%), NPDES site densities, and human waste N input rate (Figure S5). However, human waste input rate showed a negative relationship with TON concentration but a positive one with DIN concentration. Baseflow also played an opposing role in affecting TON and DIN concentrations. It appeared to dilute stream TON but increased DIN, leading to a non-monotonic relationship with TN concentration. Annual mean of vegetation greenness and precipitation were negatively associated with TON and TN concentrations, but their impact on DIN was varying. Monthly mean precipitation was positively associated with TON concentration but negatively with TN concentration.

For high input watersheds, one of the most important predictors of DIN and TN concentrations was baseflow contribution, which was positively associated with DIN and TN concentrations (Figure 3e & S6). In contrast, baseflow contribution had a negative relationship with TON concentration. Similarly, wetlands also affected N forms in different ways: increasing wetland coverage was associated with decreasing stream DIN and TN concentrations but increasing TON concentration (Figure 3e & S6). Predictors related to human activities were also crucial in the high N input sub-models. Crop N fixation rate was the most important predictor for TN concentration probably due to its positive association

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with agricultural practices, rather than because it was the ubiquitously most important source of high N inputs in these watersheds. Monthly mean fire numbers had a positive relationship with TON but a negative relationship with DIN concentration.

Environmental Implications

N inputs establish spatial patterns of stream N concentrations

Watershed N inputs alone explained approximately half of the spatial variation in stream TN concentrations, like a previous finding of 47%[38]. Spatially explicit models[45] of seasonal nutrient concentrations across the US also uncovered spatial patterns similar to our findings, but these models did not include nutrient inputs, and yielded correlation coefficients ranging between 0.61 and 0.78, thus explained 37-61% of the variation in TN concentrations. Our model results based on all sample sites explained 58-70% of the variation in stream N concentrations, affirming that model predictive power may be improved by including watershed-specific and time-specific nutrient inventory variables.

Recent studies[26,46] demonstrated that temporal variations in hydrological nutrient export were largely controlled by hydrological factors, but the spatial patterns were better predicted by nutrient inputs. Our results support the finding that inputs drive the spatial patterns. Spatial variations and relationships between N inputs and stream concentrations are thought to be somewhat stable over time[47], which in part could be related to time lags and nutrient legacies[48,49], and relatively static land cover and inputs over the recent decade[31]. The long-term imprint of high N inputs, largely from agricultural sources, has proven challenging to erase over time despite many years of efforts to reduce the release of N.

Impact of N inputs on stream N speciation and watershed retention

The speciation or forms of stream N varied with N input level. Stream TN was dominated by reduced N, especially TON in areas with low N inputs. This was probably due to wetland contributions of organic N in these watersheds. But NO_3/TN ratio increased significantly with enhanced N inputs (Table 1a & Figure 2a). The elevated level and proportional contribution of in-stream NO_3 as N inputs increase supports N saturation theory, where organic N dominates in less disturbed watersheds, but stream NO_3 export increases with added inputs as terrestrial and aquatic ecosystems lose their ability to retain added N[50–54].

Our work provides new insights about the factors leading to watershed N saturation and changing stream N forms. The stronger and steeper relationship between stream TN concentration and N input rate in NO_3-dominated streams (Figure 2b & S3) suggests that NO_3-dominated streams respond more strongly to further N inputs and become more saturated at a faster rate than the ‘reduced’ group. Therefore, increasing nutrient inputs not only affects immediate aquatic nutrient level and speciation, but can also alter long-term nutrient cycling by limiting N retention capacity in some watersheds and exacerbating nutrient loss and aquatic eutrophication.

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Impact of climate and landscape drivers

While spatial variation of stream N concentrations corresponds closely to patterns of N inputs and sources[26], there remains substantial scatter around this relationship[38,55,56]. Many factors can affect watershed nutrient dynamics and stream nitrogen concentrations, including hydrology, soils, and geology[46,57–59]. Random forest modeling validated that a complex variety of climate and physical watershed features can interact to drive instream N concentrations across the CONUS.

The relationship between hydrology and nutrient concentration can help interpret the interaction between the role of transport (precipitation) and supply (nutrient source)[60]. In low N input watersheds, stream DIN concentration increased with both monthly mean precipitation and deposition input rate, demonstrating that wet deposition was an important source of DIN in these systems. On the other hand, in watersheds where monthly mean precipitation was > 100 mm, stream TON decreased with increasing monthly mean precipitation, indicating dilution of the organic N source by precipitation and/or the importance of baseflow input to the summer stream flow (Figure S4).

Separating the influence of summer mean precipitation from deposition and total N inputs is confounding since all three increase from west to east. This spatial gradient could be driving the apparent negative association between stream TN and monthly mean precipitation in the medium N input group: watersheds in the Plains and Lowlands region on average had lower monthly mean precipitation but higher N input rate compared to the eastern watersheds. For the high N input group, the majority (> 65%) of sites were located in the Plains and Lowlands region, and concentrations of TON, DIN and TN all increased with monthly mean precipitation, suggesting these systems were transport limited rather than (N) supply limited[60]. Positive relations between hydrology and stream N concentration are typical for agricultural watersheds, which may result from increased soil leaching and surface runoff during periods of high rainfall and associated elevated flows from agricultural tile drainage[59].

Wildfires can have large impacts on water quality and the aquatic ecosystem by altering stream nutrient species and concentrations[61–63]. The positive relationship between monthly mean fire counts and N concentrations (when > 1 fire within 1000km^2 per day) suggested elevated post-fire N transport to streams, either via transport of N from the soil and forest floor or via increased ash and atmospheric deposition[64]. The impact of wildfires on reorganizing watershed N cycling is a complex process. For example, severe wildfires could change forms of organic N by converting it to the more soluble form or volatilize N[61,65]. How fast forest systems can recover from fires also affects stream N concentrations[62,63,66]. More careful separation of the drivers is required to conduct a more definitive analysis on wildfire impact.

Two critical landscape factors also interacted with N inputs to shape stream TN: wetland cover and the ratio of baseflow to total flow (i.e., the baseflow index)[67]. By dividing and modeling N concentrations at three levels of N inputs, we revealed that the context of N input can influence these relationships.

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Wetlands play important but varying roles—Wetlands can behave as a potential source of dissolved organic N[68,69]. In the previous examination of the NRSA 2008-2009 survey period, TON was positively correlated with the proportion of wetland in the watershed, and our findings reinforce this finding[38]. The net effect on TN concentrations depends on wetland conditions[70,71].

Covarying spatial gradients across the CONUS in wetland distribution and N input contributed to the positive relationship between wetland coverage and stream TN concentration in low input watersheds. Watersheds in the plains, especially the coastal plains and upper Midwest regions, had the highest wetland coverages and the greatest input rates. In general, watersheds in the Western Mountains had the lowest wetland coverage and N input level. Smith et al.[72] also identified this spatial gradient in natural background stream TN concentration across the CONUS. More analyses are needed to separate the impact of nutrient gradients confounding with gradients in land uses. However, in the Eastern Highlands region, especially the Appalachians, stream TN concentration in low input watersheds had a positive relationship with wetland coverage, whereas N input rates decreased with increasing wetland coverage, indicating the importance of wetland to stream nutrient level (Figure S7).

The negative association of wetland cover with stream DIN and TN concentration in high N input watersheds (Figure 3e) supports previous work on the strong N removal potential of wetlands if they are present and hydrologically connected[73–75]. Wetlands were also an important source of TON in high N input sites (Figure S6). Increasing wetland coverage was accompanied by decreasing agricultural land coverage in many regions, hence often coincided with lower watershed N input rate. But wetlands can serve as a sink of stream TN through denitrification even though wetland N retention rate varies by region and site[76]. We found that some NRSA watersheds with the highest N input rate (>100 kg N ha^{-1} yr^{-1}) and high wetland percentages (> 10%) had TN concentration < 2 mg N L^{-1} or even < 1 mg N L^{-1}, indicating the effectiveness of wetland N retention and potential conservation efforts in these areas. For those watersheds, the location of wetlands in flow paths and in relation to the N input source regulate their ability to serve as removal barriers to excess nitrogen[74].

Proportion of baseflow: An indicator of legacy groundwater contamination in high N input areas?—The impact of baseflow contribution[77] on stream N concentrations also diverged at different input levels (Figure 3d–e). The negative relationship between baseflow and stream N concentrations in low N input watersheds may indicate dilution by subsurface contributions, especially for stream TON. Denitrification along subsurface flow paths could further reduce DIN concentration in streams with high baseflow contribution[78]. In contrast, we found a positive relationship between baseflow contribution and stream DIN in high N input watersheds, suggesting that potential baseflow inputs of NO_3-contaminated groundwater contributed to stream N in these watersheds. We also found a negative relationship between baseflow contribution and TON concentration in these high N input watersheds, indicating that baseflow might also serve as a dilution of TON, likely as a result of mineralization of TON along the flow path and/or low efficiency of subsurface transport of dissolved organic matter controlled by sorption processes[79–82]. NO_3/TN ratios were > 0.95 at some high TN concentration sites (>10 mg N L^{-1}), confirming the subsurface source

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of N. Watersheds with long agricultural histories and high nutrient input can experience nutrient legacies, which potentially accumulate in soil and groundwater over decades of excess fertilizer application, acting as a long-term source that slowly releases N into surface waters and can hinder nutrient reduction efforts[48,83]. Our findings support the hypothesis that groundwater sources critical to summer low flows can be contaminated with excess N in high N input areas, where streams are more vulnerable to legacy N contamination[84].

Model implications

By careful quantification of N inputs combined with the random forest approach to tease out relationships by N input level, we were able to identify context-dependent connections. Critical variables may have diverging impacts on stream chemistry depending on climate, hydrology, and long-term land use history, and can lead to either improving or degrading water quality.

The long-term trajectory of N inputs is important to consider – decades of high N inputs in some areas may lead to a very complex N input-output relationship. Where groundwater is contaminated with NO_3, and baseflow is an important component supplying streamflow, thus N export may be driven by NO_3 inputs from baseflow that reflect legacy N inputs and preferential leaching of mobile NO_3. This interaction between legacy N inputs and groundwater contamination provides continued challenges to reducing stream N loads and concentrations[83,85–87]. By coupling information about baseflow proportion, current and legacy N inputs, and stream N concentrations and fluxes, it may be possible to identify these streams with shorter and longer timeframes for recovery and include this information in environmental decision making.

Limited resources are available for watersheds restoration and assessment. Spatially explicit datasets on watershed characteristics and water quality models can provide critical support to help evaluate the success of N reduction efforts. A recent study, by applying spatial records on nutrient inventory, identified key areas to boost nutrient use efficiency and to achieve biggest gains to water quality restoration[88]. Our high-performing random forest models can be applied to efficiently make predictions of stream N concentrations in all NHD streams in the CONUS, and interpolate water quality information for areas lacking in data. This next-step application of our models will provide managers with valuable insights to prioritize monitoring efforts (such as groundwater/baseflow monitoring), identify key spots for effective actions in the absence of additional in-situ measurements, and design N reduction strategies within or across different regions.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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in this paper are those of the authors and do not necessarily reflect the views or policies of the USEPA. Dataset for this study has been submitted to the USEPA data repository and will be publicly available upon approval at: doi:10.23719/1519428. Code for random forest modeling has been submitted as part of the Supporting Information.

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Synopsis

Watershed nitrogen inputs drive stream nitrogen concentrations and forms, while climate, hydrology, and land cover are also influential

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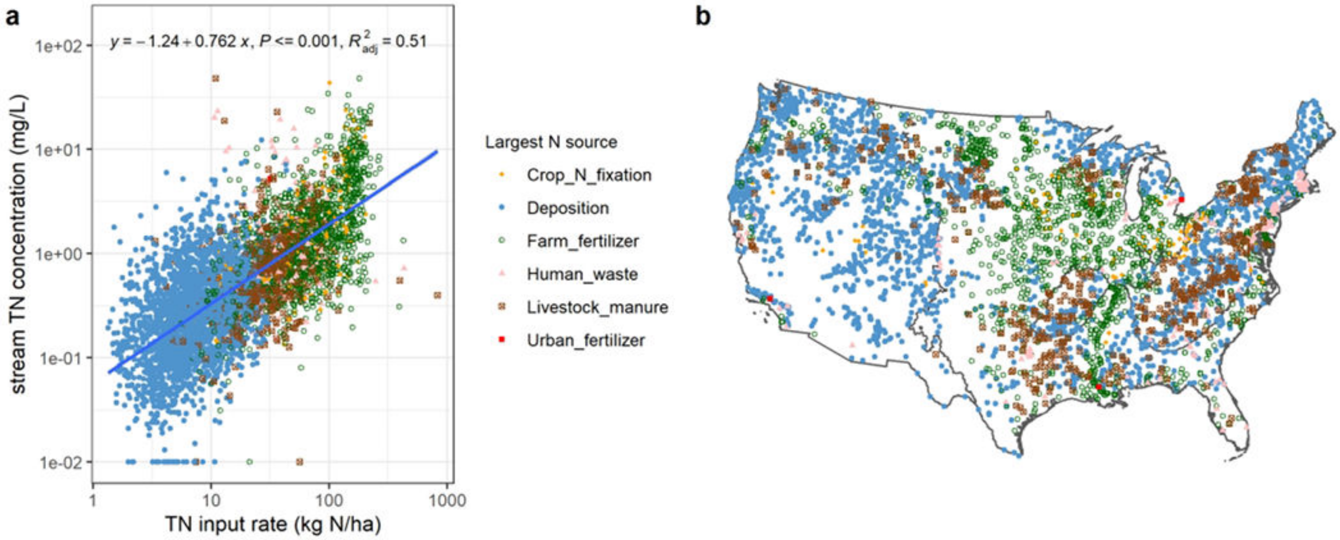

Figure 1.

a. Stream TN concentrations and largest N sources across the CONUS; colors and shapes represent different largest landscape TN sources. b. Stream TN concentrations as a function of N inputs; colors and shapes represent different largest landscape TN sources. Lines are the three regions' boundaries (Figure S1).

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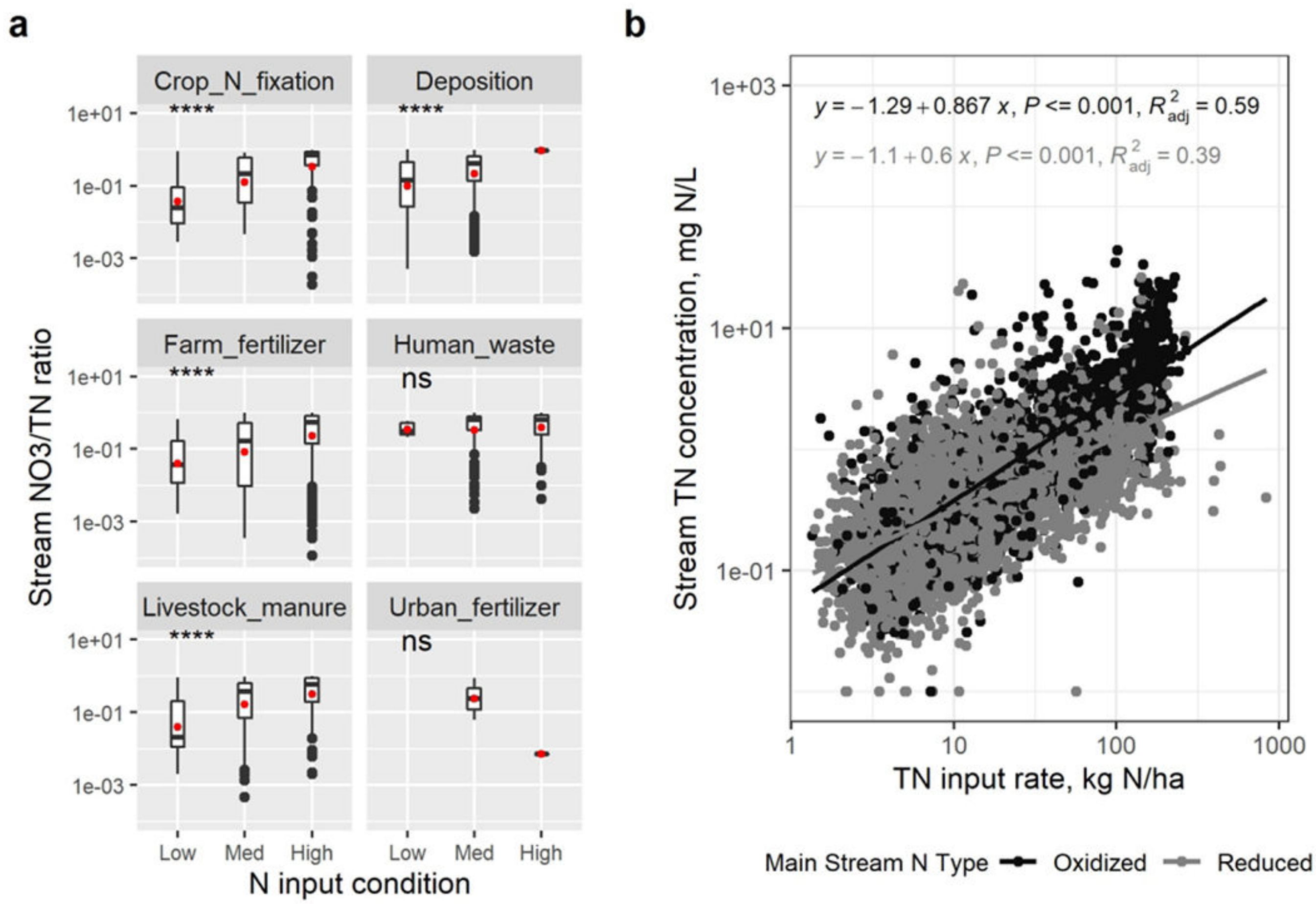

Figure 2.

a. Comparing stream NO3 contribution at three input levels and in watersheds with different larges N sources. Red points indicate group means. ****: p <= 0.0001; ns: not significant.

b. Stream TN concentrations as a function of N inputs; colors represent the main N species (‘oxidized’-black vs ‘reduced’-grey).

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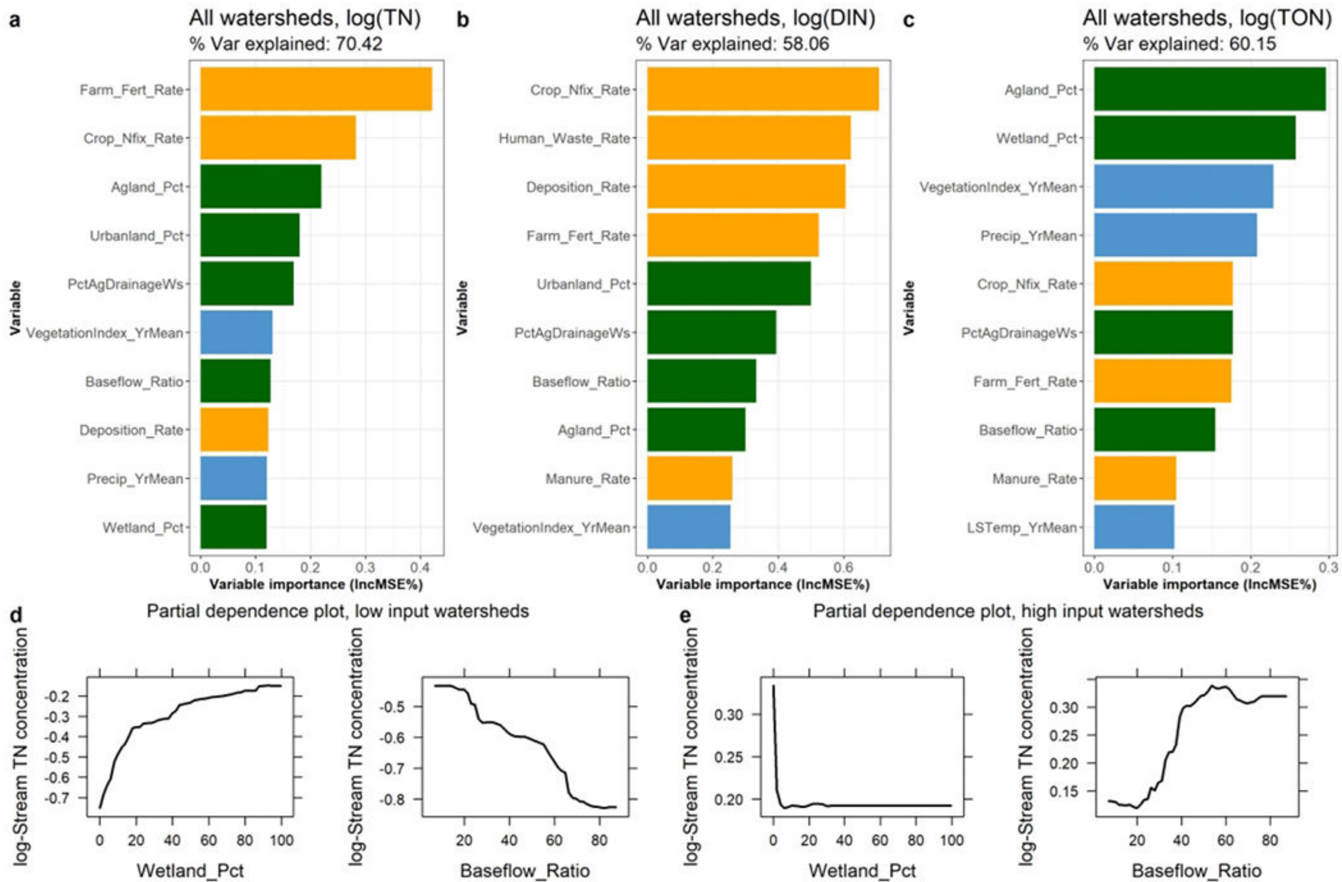

Figure 3.

Variable importance plots of random forest model results for a) stream TN concentration; b) DIN concentration, and c) TON concentration. Each model combined data from three surveys (n = 4997). Only the top 10 variables were plotted. Bar colors represent different predictor categories: Green—StreamCat landscape and land use (%) variables; Blue—climatic variables; Orange— N input rates of six sources. The partial dependence relationships of stream TN concentration vs. wetland coverage and baseflow contribution in low input watersheds (d) exhibited opposite trends with those in high input watersheds (e).

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Table 1.

a. Means and standard errors (SE) of watershed N input rate, stream N concentrations, NO3/TN ratio, and TON/TN ratio of a. watersheds of different land use types and input levels, and b. different regions and stream N types. n = number of streams.

a

Watershed type	Input level	N input rate (kg N ha^{-1})	Stream TN (mg N L^{-1})	Stream NO3 (mg NL^{-1})	Stream TON (mg NL^{-1})	Stream NO3/TN ratio	Stream TON/TN ratio	n
		Mean (SE)						
Agriculture	Low	10.50 (0.25)	0.60 (0.14)	0.21 (0.13)	0.38 (0.03)	0.13 (0.02)	0.83 (0.02)	134
	Medium	32.76 (0.31)	1.10 (0.04)	0.44 (0.04)	0.62 (0.02)	0.33 (0.01)	0.63 (0.01)	895
	High	104.85 (1.54)	3.16 (0.13)	2.21 (0.11)	0.85 (0.04)	0.51 (0.01)	0.45 (0.01)	1132
	All	69.14 (1.15)	2.15 (0.07)	1.35 (0.07)	0.72 (0.02)	0.41 (0.01)	0.55 (0.01)	2161
Deposition	Low	6.93 (0.08)	0.39 (0.01)	0.11 (0.01)	0.27 (0.01)	0.25 (0.01)	0.71 (0.01)	2080
	Medium	22.52 (0.26)	0.71 (0.04)	0.33 (0.03)	0.34 (0.02)	0.40 (0.01)	0.55 (0.01)	577
	High	60.69 (3.48)	2.31 (0.16)	2.14 (0.21)	0.16 (0.05)	0.92 (0.03)	0.07 (0.02)	2
	All	10.36 (0.15)	0.46 (0.01)	0.16 (0.01)	0.28 (0.01)	0.28 (0.01)	0.67 (0.01)	2659
Human	Low	12.15 (0.69)	12.78 (4.07)	3.84 (1.12)	1.40 (0.66)	0.37 (0.07)	0.16 (0.06)	5
	Medium	33.77 (0.86)	1.93 (0.32)	1.51 (0.31)	0.37 (0.02)	0.55 (0.03)	0.41 (0.03)	93
	High	82.69 (5.43)	1.99 (0.27)	1.33 (0.24)	0.50 (0.04)	0.54 (0.03)	0.40 (0.03)	79
	All	54.99 (3.10)	2.26 (0.27)	1.50 (0.20)	0.46 (0.03)	0.54 (0.02)	0.40 (0.02)	177

b

Regions	Stream N type	N input rate (kg N ha^{-1})	Stream TN (mg N L^{-1})	Stream NO3 (mg NL^{-1})	Stream TON (mg NL^{-1})	Stream NO3/TN ratio	Stream TON/TN ratio	n
				Mean (SE)				
Eastern Highlands	Oxidized	36.02 (1.02)	1.24 (0.08)	1.00 (0.08)	0.22 (0.01)	0.71 (0.01)	0.26 (0.00)	642
	Reduced	24.14 (1.50)	0.47 (0.02)	0.11 (0.00)	0.32 (0.02)	0.25 (0.01)	0.69 (0.01)	667
	All	29.97 (0.93)	0.85 (0.04)	0.55 (0.04)	0.27 (0.01)	0.47 (0.01)	0.48 (0.01)	1309
Plains and Lowlands	Oxidized	91.89 (2.20)	3.95 (0.18)	3.33 (0.16)	0.57 (0.03)	0.76 (0.01)	0.22 (0.00)	726

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a

Watershed type	Input level	N input rate (kg N ha^{-1})	Stream TN (mg N L^{-1})	Stream NO3 (mg NL^{-1})	Stream TON (mg NL^{-1})	Stream NO3/TN ratio	Stream TON/TN ratio	n
		Mean (SE)						
	Reduced	43.71 (1.10)	1.08 (0.04)	0.15 (0.01)	0.84 (0.03)	0.13 (0.00)	0.82 (0.00)	1593
	All	58.80 (1.12)	1.98 (0.07)	1.14 (0.06)	0.76 (0.02)	0.33 (0.01)	0.63 (0.01)	2319
Western Mountains	Oxidized	11.55 (1.09)	0.78 (0.08)	0.61 (0.07)	0.16 (0.02)	0.69 (0.01)	0.27 (0.01)	312
	Reduced	7.10 (0.42)	0.31 (0.03)	0.05 (0.01)	0.22 (0.01)	0.13 (0.00)	0.82 (0.00)	1057
	All	8.11 (0.41)	0.42 (0.03)	0.18 (0.02)	0.21 (0.01)	0.26 (0.01)	0.69 (0.01)	1369