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Trends in Drinking Water Nitrate Violations Across the United States

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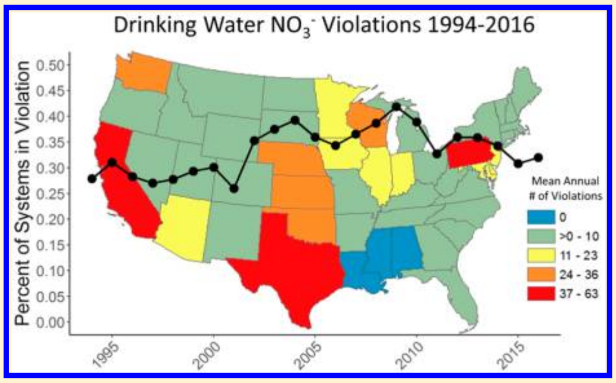
Supporting Information

ABSTRACT: Drinking water maximum contaminant levels (MCL) are established by the U.S. EPA to protect human health. Since 1975, U.S. public water suppliers have reported MCL violations to the national Safe Drinking Water Information System (SDWIS). This study assessed temporal and geographic trends for violations of the 10 mg nitrate-N L^{-1} MCL in the conterminous U.S. We found that the proportion of systems in violation for nitrate significantly increased from 0.28% to 0.42% of all systems between 1994 and 2009 and then decreased to 0.32% by 2016. The number of people served by systems in violation decreased from 1.5 million in 1997 to 200 000 in 2014. Periodic spikes in people served were often driven by just one large system in violation. On average, Nebraska and Delaware had the greatest proportion of systems in violation (2.7% and 2.4%, respectively), while Ohio and California had the greatest average annual number of people served by systems in violation (278 374 and 139 149 people, respectively). Even though surface water systems that serve more people have been improving over time, groundwater systems in violation and average duration of violations are increasing, indicating persistent nitrate problems in drinking water.



2. INTRODUCTION

Clean drinking water is essential for the health and well-being of humans and life on Earth.[1] Drinking water mainly originates from surface water (lake, reservoir, river, stream) or groundwater in the U.S.[2] Human activities such as fertilizer use, manure application, and sewage treatment can contaminate sources of drinking water with nitrate, which can easily leach through soil into groundwater and surface water.[3] Numerous studies indicate significant contamination of groundwater by nitrate across the U.S., particularly in shallow or unconfined groundwater wells underlying agricultural areas with high levels of fertilizer use and well-drained soils.[3b,4]

There are a variety of anthropogenic point and diffuse sources of nitrogen, including atmospheric deposition,[5] wastewater treatment plants,[6] leaking or poorly managed septic systems,[7] leaky urban sewers,[8] urban runoff,[9] fertilizer,[10] and animal waste.[11] The largest contributor to landscape N inputs in the U.S. is through agriculture, including synthetic fertilizer application, land application of manures from concentrated animal feeding operations (CAFOs), and crop N fixation.[11] Fertilizer nitrogen inputs have increased food production,[12] but excess nitrogen in the environment has decreased biodiversity,[13] increased coastal eutrophication,[14] and created potentially fatal human health risks.[15]

Numerous studies show that nitrate in drinking water can have serious human health consequences. Excess nitrate in drinking water can cause methemoglobinemia (blue baby syndrome).[16] Nitrate contamination in drinking water may be associated with certain cancers,[17] birth defects,[18] and thyroid issues,[16] though the results of these studies have been varied.[19]

The objective of this research was to analyze the temporal and geographic trends in drinking water nitrate violations across the conterminous U.S. (CONUS). The specific goals were to analyze (1) the number and proportion of systems with violations per year, (2) the number of people served by systems in violation per year, (3) the duration for systems in violation, (4) violations by water source (groundwater vs surface water), and (5) how violations vary geographically.

3. MATERIALS AND METHODS

3.1. Background and Data Sources. *3.1.1. Sources and Treatment of Drinking Water.* About 86% of the U.S. population obtains their water from a public water system (PWS); the other 14% gets their water from a private source, typically unregulated domestic wells.[2] A PWS is any system that provides water for human consumption with at least 15 service connections or that regularly serves an average of 25 or more individuals daily at least 60 days per year.[20] There are over 150 000 active PWSs in the U.S.,[20a] which can be publicly or privately owned. A PWS obtains its drinking water from surface water (SW) and/or groundwater (GW) sources; accounting for 66% and 34% of the population served by PWSs, respectively.[21]

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Some PWSs receive water from both surface and groundwater; designation as a SW or GW system is based on major water source.

3.1.2. EPA's Safe Drinking Water Information System. The U.S. Environmental Protection Agency's (EPA) Safe Drinking Water Information System (SDWIS)[22] collects data for all PWSs, including violations for contaminants regulated under the Safe Drinking Water Act. SDWIS provides publicly available violation information for over 90 contaminants, including total coliform, disinfection byproducts, arsenic, heavy metals, radionuclides, inorganic chemicals, and nitrate.[22]

U.S. PWSs obtain their water from one or more facilities (Supporting Information (SI) Figure S1). SDWIS drinking water facilities can be a cistern, intake, pump facility, spring, storage, treatment plant, well, or other.[22] A PWS is characterized as a community water system (CWS), a nontransient noncommunity water system (NTNCWS), or a transient noncommunity water system (TNCWS).[20b] A CWS is a PWS which "serves at least 15 service connections used by year-round residents or regularly serves at least 25 year-round residents."[20b] A NTNCWS is a non-CWS "that regularly serves at least 25 of the same persons over 6 months per year."[20b] Examples are schools, factories, office buildings, and hospitals which have their own water systems.[23] A TNCWS is "a non-CWS that does not regularly serve at least 25 of the same persons over six months per year."[20b] Examples include highway rest stops and campgrounds.[23]

3.1.3. Nitrate Drinking Water Regulations. PWSs have reported drinking water violations for nitrate since 1978. Since January 1, 1993,[24] PWSs are required to monitor drinking water for compliance with the maximum contaminant level (MCL) for nitrate (10 mg N L^{-1}) and are required to report violations of the MCL to the state and EPA.[24] PWSs served by groundwater must sample once annually for nitrate, while PWSs served by surface water must monitor quarterly for nitrate (except for TNCWSs, which must monitor annually). However, surface water systems that have four quarters at less than 50% of the MCL can sample annually.[24] The frequency of sampling increases to quarterly for at least one year for all PWS types if any one sample is found to be ≥50% of the MCL.[20b] Both groundwater and surface water systems are required to take a minimum of one sample at every entry point to the distribution system (Figure S1). Prior to 1993, surface water was sampled annually and groundwater was sampled every three years for nitrate.[25]

3.2. Analysis of Data. Data on nitrate MCL violations across the CONUS were downloaded from the SDWIS database[22] and uploaded into the R statistical software[26] for processing and analysis. Using the year and quarter the violation occurred, and information on PWS water source, type, and ownership, we computed a variety of metrics, including (Table S1): number and percent of systems in violation per year, number and percent of people served by systems in violation per year, average and maximum duration systems were in violation, percent of first time and repeat violators, concentration above the MCL, and number and percent of monitoring/reporting (MR) violations for nitrate (a failure to monitor and/or report water sampling results). We used the state and county served by each PWS to calculate how nitrate violations vary geographically across the CONUS (SI Table S1). We also examined violation rates in 2014 and 2016 based on treatment in the prior years to see if changes in treatment between years effected violations. Details on how each violation metric was calculated are in Table S1.

Before analysis we filtered the data temporally, geographically, and by nitrate species. We analyzed years 1994–2016 because regulations have been consistent since January 1, 1993, and inventory data was only available for 1994–2016. SDWIS has data for all nitrogen species: nitrate, nitrate–nitrite, and nitrite, with 10 428 systems in violation of the nitrate MCL, 1,922 systems in violation for nitrate–nitrite (same MCL as nitrate), and 154 systems in violation for nitrite (MCL of 1 mg nitrite-N L^{-1}) from 1994 to 2016. We excluded nitrite violations to focus on nitrate and nitrate-nitrite violations (hereafter "nitrate"). To test for significance in temporal trends, we used the nonparametric Mann-Kendall test, due to non-normal and nonhomogeneous model residuals. Also, we used the nonparametric and unbiased Sen's slope method to estimate linear regression coefficients.

One caveat with this analysis is that nitrate monitoring is inconsistent across the states and there is potential for underreporting of violations.[20b] For example, under certain conditions, at the discretion of the state, some non-CWSs can have an MCL of 20 mg N L^{-1}.[20b] There have only been six states listed as violating a 20 mg N L^{-1} MCL. Discretionary reporting would result in our underestimating the number of systems violating the 10 mg N L^{-1} MCL. As such, the results of this study are conservative. Also, it is possible there were PWSs in violation that did not report or failed to monitor, in which case, nitrate levels are not known.[27] When this occurs the PWS is listed as having a MR violation. By looking at MR violations, we were able to assess the potential influence of not monitoring or reporting nitrate violations, such as if certain states or regions systematically have MR violations.

It is important to note that SDWIS provides the population served for each PWS (updated at the discretion of the state), but not the number of people served for each facility within a PWS. SDWIS does not report which facility is in violation, only whether the whole PWS is in violation. If a PWS is in violation and there are multiple facilities, only that fraction of the population being served water by the facility that tested above the MCL is affected (Figure S1) unless the system mixes its water sources prior to entry into the distribution system. Therefore, the population served by the PWS cannot be considered the same as people exposed to a contaminant above the MCL. Additionally, calculations of population served include both CWSs and non-CWSs, and because residents of CWSs may also use water from non-CWSs, there can be some double counting of people served; based on results described below, this is 7% or less of the population. Also, the number of violations by water source, PWS type, or owner type each year are based on current information in SDWIS. SDWIS does not provide information on whether types have changed before 2013, but they can change.

To assess how well nitrate violations at the county level could be explained by landscape and geologic factors, we ran a logistic regression model using several variables that have been found by others[28] to influence nitrate in groundwater and surface water. We calculated the response variable as the binary: violations or no violations for each CONUS county for the 1994–2016 period. The predictor variables were the percent of land within the county with man-made agricultural drainage,[29] percent developed land,[30] percent cultivated land,[30] permeability of soils,[31] water table depth,[31] soil organic matter content,[31] 30-year normal mean precipitation,[32] and several variables used by Nolan and Hitt[28] in their national nitrate model: nitrogen from fertilizer inputs, animal manure, Hortonian overland flow, population density, and presence or absence of semiconsolidated sand aquifers.[33] All variables were summarized at the county level using ArcGIS. We also compared means and 95% confidence intervals for the predictor variables used in the logistic model for counties with and without violations.

4. RESULTS

Out of all regulated contaminants with MCL violations data in SDWIS, nitrate had the most prevalent MCL violation from 1994 to 2004; since then, nitrate is still one of the top three to four MCL violators each year (Figure S2a). From 1994 to 2016, the number of nitrate violations went from 57% to 17% of all drinking water violations (SI Figure S2b). This shift is driven by an increase in other contaminant violations, due to new regulations in the early 2000s.[20b]

4.1. Temporal Trends for Systems in Violation for Nitrate. There was an increase overall in the proportion of systems in violation of the nitrate MCL from 1994 to 2016 (p = 0.04, slope = 0.003); within this trend there is an increase from 1994 to 2009 ($p < 0.01$, slope = 0.009), and a decrease from 2009 to 2016 (p = 0.01, slope = −0.01, Figure 1). The analysis was broken into two time periods based on the peak in numbers of systems in violation. The number of systems in violation of the nitrate MCL increased from 476 to 643 systems between 1994 and 2009 ($p < 0.01$, slope = 10.6) and decreased from 643 to 483 systems between 2009 and 2016 (p = 0.02, slope= −23); but there was no change overall from 1994 to 2016 (p = 0.24, slope = 3.2, Figure 1a). The average concentration in samples exceeding the MCL was 22 mg N L^{-1} and was relatively stable from 1994 to 2016 (SI Figure S3). While there has been an increasing trend in the proportion of systems in violation at the national level, some states showed an increase (e.g., Texas and California), whereas other states showed a decrease (e.g., Oklahoma and Pennsylvania; SI Table S2). A possible reason for the decline in some states may be that the percent of all active systems with nitrate removal technologies increased from 13.9% to 15.0% (20 803 to 22 122 systems) between 2014 and 2016 (SI Table S3). However, in 2014 and 2016 there was no difference in violation rate between nitrate treatment and no nitrate treatment (SI Table S3). Yet for systems previously in violation in 2014, the presence of nitrate treatment in 2015 was associated with a significant reduction in 2016 violations, based on a Chi-squared test ($p < 0.05$); those systems had 21% fewer violations than systems without nitrate treatment (SI Table S3, Figure S4). This indicates nitrate treatment is more effective for systems previously in violation, possibly because these operators are more motivated to not violate again.

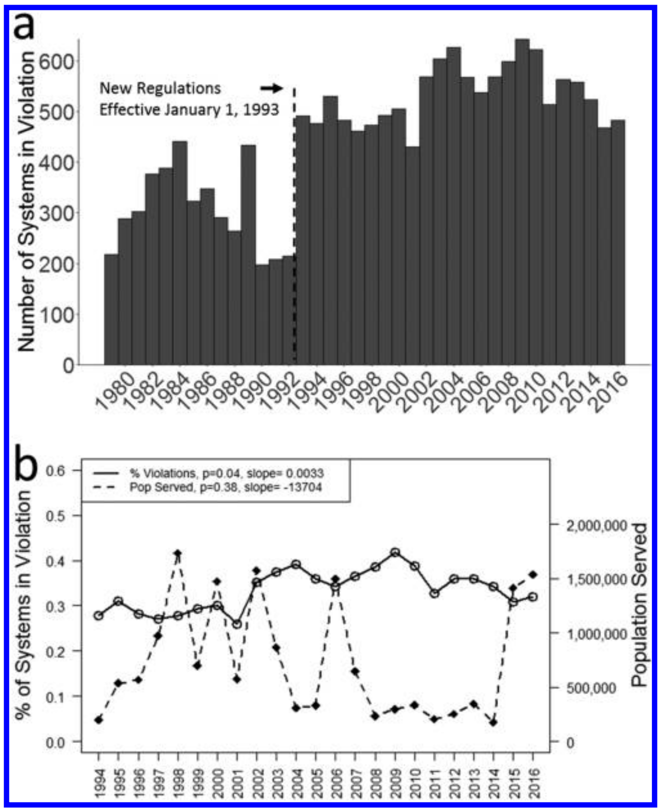

Figure 1. (a) Number of nitrate violations each year since beginning of SDWIS monitoring 1979−2016. In 1993 the regulations changed and there was an increase in sampling frequency for groundwater systems. (b) Percent of systems in violations for nitrate MCL, with population served by systems in violation for nitrate. Population served is not the same as population affected by a drinking water violation.

The proportion of repeat violators (systems that had at least one previous violation) increased from 51% in 1994 to 80% in 2014 and 74% in 2016 ($p < 0.01$, slope = 8.9, Figure 2a). In addition, the average consecutive period of time a system was in violation for nitrate increased from 0.33 yr to 0.62 yr from the 1994−1996 period to the 2012−2014 period ($p < 0.01$, slope = 0.01, Figure 2b). In fact, some systems have been in violation for over 10 consecutive years and these systems are typically groundwater systems (Figures 2c, S5).

The increased proportion of systems in violation for the nitrate MCL is primarily due to increases in violations by small to medium (<10,000 people served) noncommunity, groundwater systems (Figure 3a,b and SI Figures S6,S7). From 1994 to 2016, the proportion of groundwater systems with a violation increased (p = 0.02, slope = 0.005) from 0.28% to 0.34%, whereas the proportion of SW systems with a violation declined over time ($p < 0.001$, slope = −0.008) from 0.21% to 0.12% (Figure 3a). The proportion of violations for CWSs and transient non-CWSs did not increase from 1994 to 2016 (p = 0.15, slope = 0.002 and p = 0.14, slope = 0.003, respectively), while the nontransient non-CWSs increased ($p < 0.01$, slope = 0.015) from 0.28% to 0.45% (Figure 3b).

4.2. Temporal Trends for People Served by Systems in Violation. The number of people served by systems in violation for nitrate is quite variable over time, ranging from several hundred thousand to nearly two million people per year (Figure 1b). From 1994 to 2016 there was no trend in population served (p = 0.4, slope= −13704, Figure 1b). However, there were several large spikes in the number of people served between 1994 and 2016, with a spike defined as violations where >50% of the served population for a particular year was from a single system. The systems causing spikes in people served are community water systems (Figure 3c,d). Five of the spikes were from the same surface water PWS in Columbus, Ohio and another in 2002 was from a single groundwater system in violation in Long Island, New York (Figures 1b and 3c,e,f). Excluding these six spikes in population served and spikes from several other systems, there is a significant decline in population served from 1994 to 2016, with

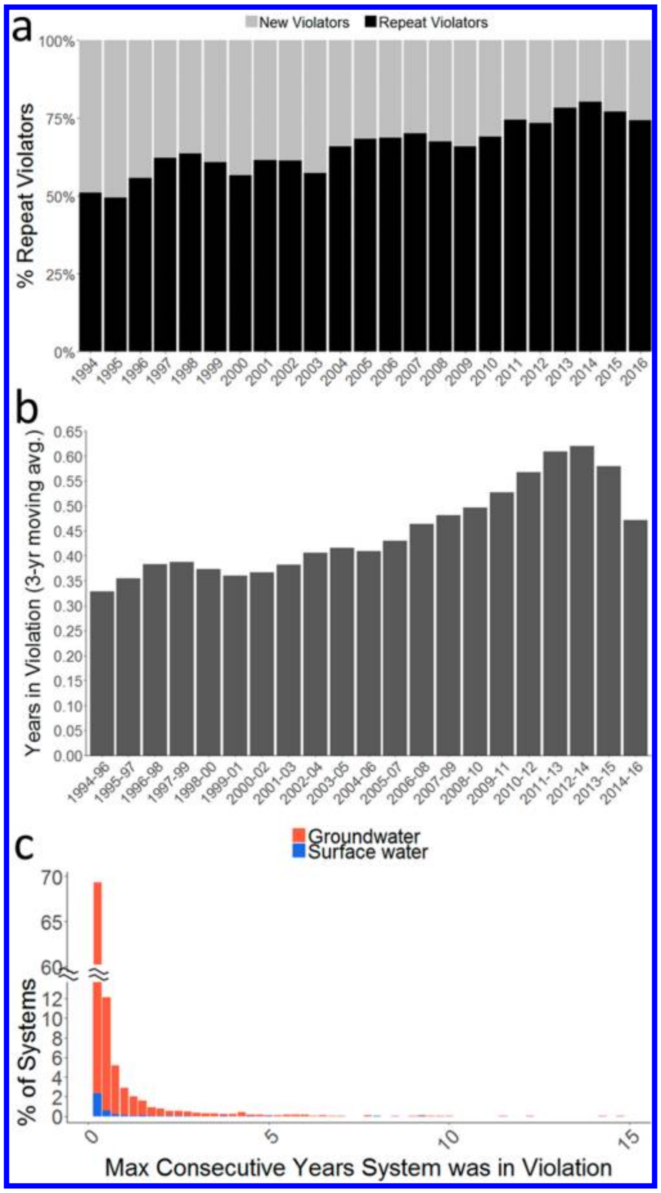

Figure 2. (a) The percent of repeat violators, (b) 3-year moving average length of time a system was in violation, and (c) the distribution of the maximum consecutive years systems are in violation.

population served declining by almost a third ($p < 0.01$, slope = −16892, Figure 3e).

4.3. Number of Violations vs. People Served. From 1994 to 2016 about 95% of all nitrate violations occurred in groundwater systems and 5% in surface water systems. However, 35% and 65% of people served by systems in violation are on groundwater and surface water systems, respectively (SI Figure S8a,b and Table S4). About 38% of PWSs in violation are CWSs and the rest are noncommunity systems, however, most people served by systems in violation (93%) are served by CWSs (SI Figure S8c,d, Table S4). Most of the PWSs in violation are privately owned (69%) and about a quarter are owned by the local government (SI Figure 8e, Table S4). However, about 86% of the people served by systems in violation are served by local government owned systems (SI Figure S8f, Table S4).

When comparing median number of people served, surface water systems serve an order of magnitude more people (870) than groundwater systems (99 people, Figure S6a) and CWSs have a greater number of people served (231) compared to TNCWSs and TCWSs (100 and 50 people, respectively, SI Figure S6b). Also, 82% of all violations are from small systems serving populations less than 500 (SI Figure S7). However, for groundwater systems, the systems with the most violations and longest duration of violations are not small systems (e.g., <500 people), but are the intermediate sized systems (500 to 100 000 people, SI Figure S9).

4.4. Geographic Trends in Nitrate Violations. California stands out in terms of number of systems in violation and population served by systems in violation. The states with the highest mean annual number of systems in violation are California, Pennsylvania, and Texas (Figure 4a), while the states with the greatest average number of people served per year, by systems in violation are Ohio and California (Figure 4b). The states with the highest number of groundwater violations were California, Pennsylvania, and Texas, while the states with the greatest number of surface water violations were Texas and Ohio (Figure 4c,d). Nebraska, Delaware, Kansas, and Oklahoma had the highest mean annual percent of systems in violation, and the highest mean annual percent of people served were in Ohio and Nebraska (Figure 4e,f). At the county level, the areas with the highest numbers of violations are in central California, northwestern Texas, southeastern Pennsylvania, southern Delaware, northwest/southeast Washington, and portions of central plains states (Illinois, Nebraska, Kansas, Oklahoma) and Wisconsin (Figure 4g). Groundwater violations at the county level follow a similar pattern, while SW violations are generally found in the same areas as greatest GW violations (SI Figure S10). The counties with the most population served by violators are generally in southcentral California, south-central Arizona, central plains, and central Ohio, generally associated with large metropolitan areas (Figure 4h). Texas, Kansas, and Oklahoma have systems that have been in violation for the longest duration (SI Figure S5c). The states with the highest mean concentrations for samples over the MCL were California and Tennessee, with mean concentrations of 64 and 23 mg N L^{-1}, respectively (SI Figure S11). Pennsylvania and Michigan had the most monitoring and reporting (MR) violations and Arizona and Oregon had the greatest proportion of systems with MR violations (SI Figure S12).

Logistic regression results comparing counties with and without violations was able to correctly classify 74% of counties, though only 52% of counties with violations were correctly classified. Significant covariates in the logistic model were percent cultivated, water table depth, soil permeability, soil organic matter, precipitation, percent of land with man-made agricultural drainage, percent of county with semiconsolidated aquifers, population density, farm fertilizer, percent developed land, and county area (SI Table S5). Most of these variables were also significant when comparing the mean and 95% confidence intervals for these variables between counties with and without violations (SI Figure S13).

5. DISCUSSION

5.1. Increases in Systems Violating the Nitrate MCL Over Time. This is the first study to show that there has been an increase in the proportion of PWSs violating the nitrate MCL across the CONUS. 95% of violations were from groundwater and the increase in proportion of PWSs in

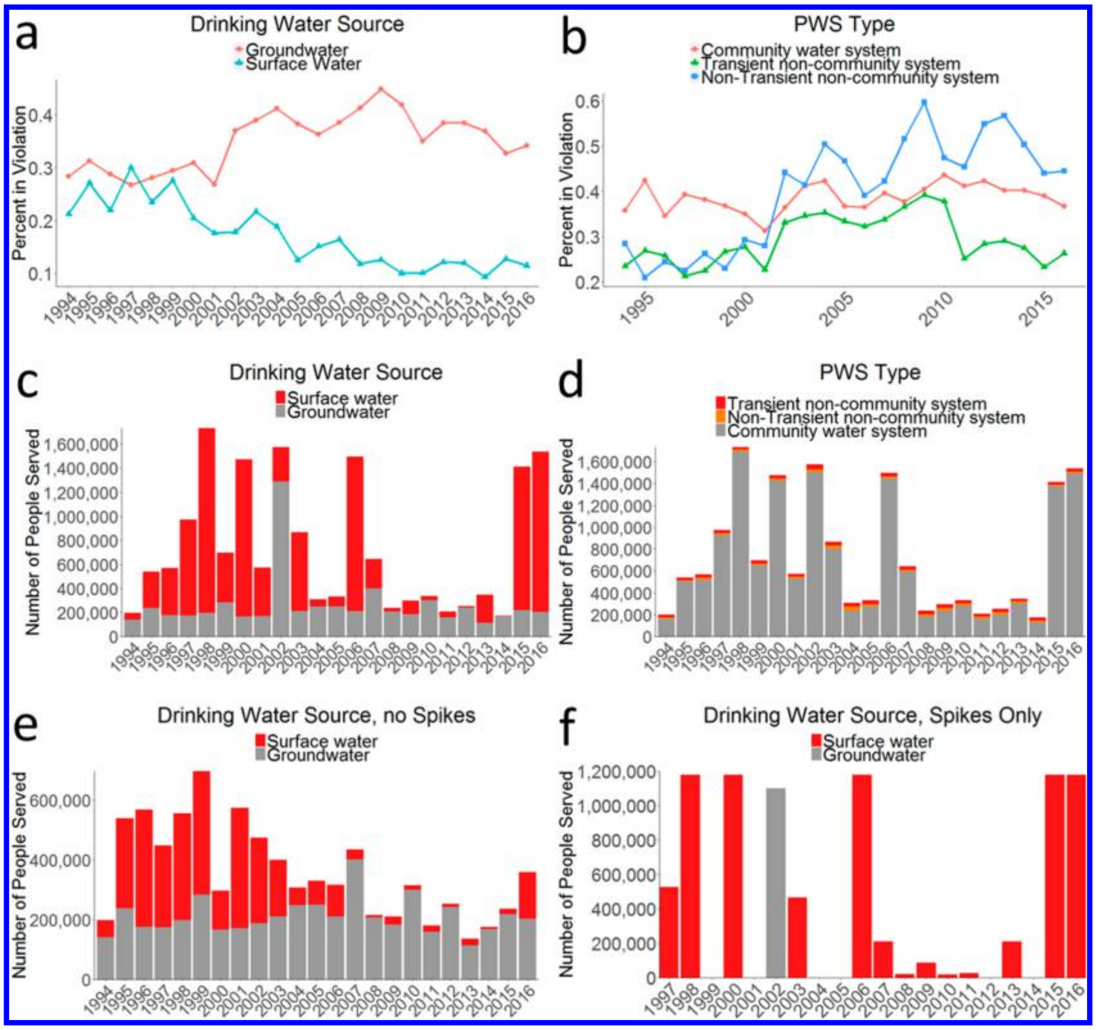

Figure 3. Percent of violations per year by (a) water source and (b) PWS type, as a percent within each category. Number of people served by systems in nitrate violation, categorized by (c) water source and (d) PWS type, and number of people served by water source (e) excluding spikes and (f) spikes only. A spike in the people served is defined as a single system contributing to >50% of the people served for a particular year. Spikes in 1998, 2000, 2006, 2015, and 2016 were caused by a single system in Ohio. Spikes in 1997, 2007, and 2013 were by three different systems in California, the spike in 2002 by a system in Long Island, and the spike in 2003 by a system in Arizona. Panel (c) is the sum of Panels (e) and (f).

violation over time was from GW, not SW systems. This finding is supported by previous work analyzing national groundwater or drinking water well data. Rupert[34] showed increases in nitrate concentrations in waters sampled in 1988−1995 and resampled in 2000−2004 in well networks across the United States, and the follow-up study by Lindsey and Rupert[35] showed a significant increase in nitrate at 21% of well networks from 1988 to 2012. In California, Burow et al.[36] found increasing trends for nitrate concentrations in groundwater in the east fans subregion of Central Valley between 1950s and 2000s. Groundwater and drinking water from the portion of the Ogallala aquifer that underlies parts of Texas, has also shown an increase in nitrate concentrations and observations above the MCL from the 1960s through the 2000s,[37] corresponding with nitrate violations found in this analysis. This previous research, along with the increasing violations for groundwater sites, suggests a need for more work to protect groundwater aquifers, since restoration of groundwater can be difficult and costly.[38]

The increase in the proportion of nitrate violations for groundwater systems may be due, in part, to the increase in N inputs nationally since the early 1900s and particularly over the last half century.[10,39] Fertilizer inputs increased from the 1940s through the 1990s nationally[10,34] and for a number of states from 1987 to 2006.[39b] The increase in N inputs from CAFOs may have also contributed to increased N violations over time.[40] And, while N deposition has declined overall, due to Clean Air Act regulations of NOx emissions,[41] deposition of ammonium has increased over time.[42]

Another reason why the proportion of nitrate violations, duration, and repeat violations have increased over time for groundwater systems may be that elevated nitrate concentrations can persist up to 60 years in groundwater aquifers, particularly those with long travel times that remain oxic and have a legacy of historical nitrate application to agricultural fields.[43] A study in Texas found that groundwater nitrate exhibits long-term persistence at intermediate and large spatial scales.[44] In fact, some Texas PWSs have the longest duration of violations for both GW and SW (Figure S5). If the nitrate source continues, the groundwater is likely to stay contaminated, but even if the nitrate source ceases it can take years for groundwater nitrate to attenuate in shallow aquifers.[45] For example, changes in irrigation and fertilizer management have resulted in declining nitrate concentrations in groundwater underlying Nebraska's irrigated cropland, but the decrease is

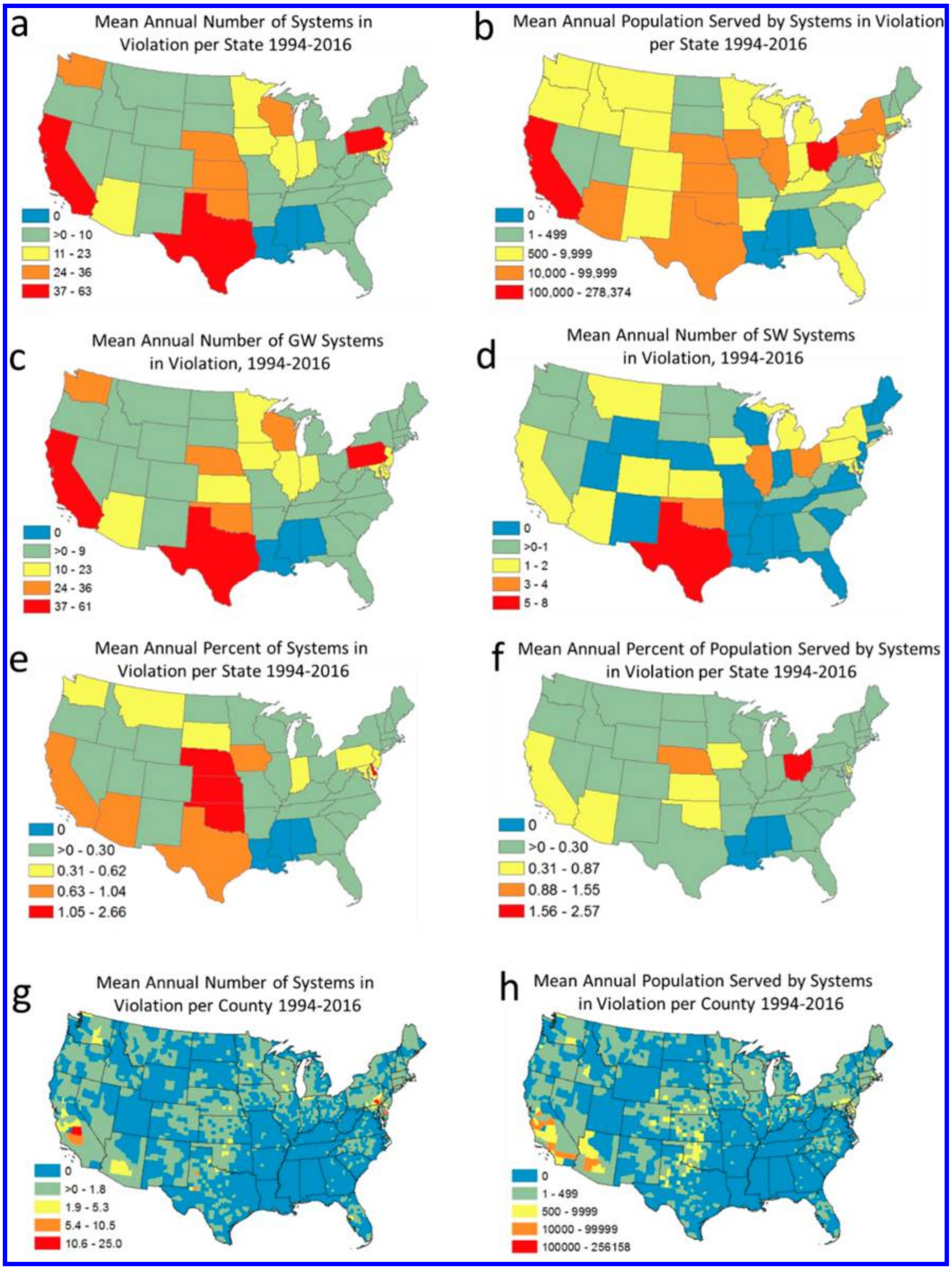

Figure 4. U.S. maps showing, by state (a) mean annual number of systems in violation, (b) mean annual number of population served by systems in violation, (c) mean annual number of groundwater systems in violation, (d) mean annual number of surface water systems in violation, (e) mean annual percent of systems in violation, (f) mean annual percent of population served by systems in violation; and by county, (g) mean annual number of violations and (h) mean annual population served by systems in violation. All numbers are based on an average of the total number of violations or population served per state or county per year from 1994 to 2016. Note that the scales are different for each panel.

slow and occurring in a limited area.[45b] Additionally, persistent nitrate contamination may be due to drinking water systems being unable to afford necessary treatment technology or to change to uncontaminated water sources.[27] This is supported by the fact that most nitrate violations (82%) are from small (<500 people served) PWSs that are primarily noncommunity, groundwater systems and are likely influenced by agricultural land use and septic systems more than the urban systems that serve larger populations (Figure 3a,b and SI Figures S6,S7).

We cannot distinguish the cause of the recent decline in the proportion of violations, from 2009 to 2016, using the data in this analysis, but there are some possible explanations, such as the recent increase in N use efficiency in the U.S. since the mid-1990s,[46] recent leveling off of fertilizer inputs[34,43d,47] the decline in wet deposition of nitrogen oxides in some areas,[5] increased carbon availability supporting denitrification,[34,43c,48] reductions in rainfall or increased drought.[49] However, because fertilizer inputs are not decreasing at a national scale, the largest factor in the decline in nitrate violations over time is likely improvements in water treatment[50] (SI Table S3) or switching of PWSs to different water sources or suppliers with lower nitrate concentrations. We caution, however, that treatment seems to work only when applied to systems that were previously in violation; for the individual years, violation rates between treated and untreated systems were similar.

5.2. Spikes in Population Served Over Time. The general decreasing trend in the population served by systems in violation for nitrate may also be due to improvements in drinking water technology by large systems, including ion exchange and reverse osmosis, or due to systems switching to or blending with different water sources.[50,51] Yet, despite these improvements, there have been periodic spikes in the number of people served by systems in violation due to isolated violations by large systems, such as the ones from a surface water system in Columbus, Ohio or the groundwater system in Long Island, New York (Figure 3c,f).

In Columbus, Ohio, the spikes in people served by a system in violation were due to nitrate contamination of the Scioto River, which receives runoff from more than 2500 km^2 of land that is 80% agriculture.[52] Heavy rains, especially when occurring soon after application of fertilizer, have caused nitrate in the Scioto River to exceed the MCL,[52a] resulting in several locally issued nitrate advisories lasting one to 3 weeks between 2000 and 2016.[52b,53] Consequently, Columbus began building a $35 million treatment plant to remove nitrate; expected to be completed in 2017.[52b] There has also been legislation in Ohio, effective August 21, 2014, on fertilizer application restrictions and requirements for farmers to receive certification on best fertilizer application practices.[54]

On Long Island, New York in 2002 there was a large spike in the number of people served by a groundwater PWS violating the nitrate MCL (Figure 3c,f). This groundwater system is the only groundwater PWS serving over 1 million people with a nitrate MCL violation; the rest of U.S. groundwater systems in violation serve 100 000 people or less (SI Figure S6a). The nitrate contamination to Long Island's groundwater is primarily from septic systems, sewage treatment plants, and current and legacy fertilizer applied on agricultural areas and suburban lawns.[55]

5.3. Geographic Locations of Violations. *5.3.1. Geographic Patterns for Number and Proportion of Violations.* The significant variables in the logistic regression model (SI Table S5) corroborate previous studies that found higher nitrate concentrations in groundwater correlated with unconfined[4a,37] and shallower groundwater depths,[3b,4c,38a,56] fertilizer use, particularly when applied above well-drained, high permeable soils,[3b,4a−d] patterns in irrigation or rainfall, and conditions that discourage denitrification (low carbon/oxidizing).[3b] States and regions where many of these factors occur together have high nitrate concentrations in groundwater,[3b,28,43a,45a,57] and correspond with areas having high numbers of nitrate violations, including the northeastern mid-Atlantic,[3b] the midwest,[45b] Texas,[4a,56b] and California.[3b,4c,57a]

The geographic patterns for nitrate violations appear to be driven by N inputs and hydrogeology. There is a good correlation between violations and the amount of fertilizer purchased and nitrogen inputs at the state and county levels (SI Table S5, Figure S13).[11,58] Specifically, Kansas and Nebraska, which had a high proportion of systems in violation, have a legacy of nitrate problems due to agriculture,[45b] and difficulty treating nitrate in rural towns.[59] In the Sumas-Blaine aquifer in northwest Washington State, 29% of wells sampled over the past 30 years exceeded the nitrate MCL,[60] and our analysis also revealed many nitrate violations here (Figure 4g). Within a study of 200 domestic wells in California's San Joaquin Valley, 42% of well samples were above the MCL, and high nitrate was associated with fertilizer and animal waste inputs.[61] In terms of hydrogeologic drivers, Pennsylvania and Delaware showed relatively high numbers of violations, corresponding with EPA estimates for the percent of state area with groundwater nitrate concentrations >5 mg N L^{-1},[62] due to well-drained soils.[3b] In nine counties within northcentral and west central Texas, nitrate has exceeded the MCL in about 50% of wells sampled.[4a,56b] In fact, the high number of violations in Texas, Oklahoma, Kansas, and Nebraska at the county level (Figure 4g) are fairly correlated with the location of the Ogallala aquifer.[56b] Shallow and unconfined aquifers like the Ogallala are not protected from infiltrating contaminants by an aquitard and can thus be more susceptible to nitrate contamination.[4a,37]

The geographic patterns for states with minimal nitrate violations may be explained by better management by the PWS, through blending, treatment, or other factors related to source water. For example, low nitrate concentrations are typically found in areas characterized by low N input, fine-textured soils,[63] tile drains,[3b] higher soil organic matter and moister conditions that promote denitrification,[4a,d] older groundwater,[64] or with high transient recharge rate of unpolluted water.[43a,45a,57b] States such as Rhode Island, New Hampshire, and Nevada, which have had a small number of violations also have less fertilizer use,[58b] but not all states follow this pattern. Some of the cornbelt states (such as Ohio and Missouri) have fewer violations than would be expected based on fertilizer use, which may be due to hydrogeology. For example, tile drainage can help prevent nitrate contamination of groundwater, yet may contribute to surface water contamination, as evidenced by Columbus, Ohio's persistent surface water nitrate problem.[3b] Additionally, there were fewer violations in southeastern states (Louisiana, Mississippi, and Alabama; Figure 4a); and this is not due to underreporting, as they have very few MR violations (SI Figure S12). Instead the lack of violations, even in agricultural areas of those states, may result from vegetative uptake and denitrification associated with wet, carbon-rich soils,[3b] and the presences of confined aquifers.[64,65]

5.3.2. Geographic Patterns for People Served. The states with the most people served by systems in violation (e.g., Ohio, California, New York, Illinois, Texas) are also states with the most surface water systems in violation (Figure 4b,d).[21,66] The mechanisms for nitrate contamination of surface water sources can be different than those for groundwater systems, though fertilizer application is still likely the largest factor for both.[67] Case studies in Ohio suggest that fertilizer can easily runoff into surface water when applied shortly before large rain events,[52a] or when there is less infiltration due to compaction,[68] frozen soils,[54,69] or use of tile drainage.[3b] Urban land use can also contribute to nitrate contamination of surface water used by PWSs serving large metropolitan populations. For example, wastewater inputs can add N to surface waters.[6,8a] Based on the county data, there is a good correspondence between high numbers of people served by nitrate violators and large cities (SI Table S5), consequently there may be greater public health implications for urban SW systems compared to rural GW systems.

5.4. Implications for Public Health and Treatment Costs. Elevated nitrate levels in water can pose both acute and long-term threats to public health. For example, high nitrate levels in drinking water are of particular concern for infants and pregnant women and can cause blue baby syndrome,[16] and prolonged exposure could increase risks for certain cancers[17] and birth defects.[18] Consequently, EPA has taken action to reduce risk through supporting reductions in nutrient loads from point and nonpoint sources, strengthening nutrient standards, and providing financial assistance to communities for drinking water treatment.[70]

When prioritizing management decisions to reduce human exposure to nitrate in drinking water, our results show that it is important for large surface water systems, serving hundreds of thousands to millions of people, to either have proper treatment technologies or be able to switch to other drinking water sources to prevent large spikes in people potentially served by systems in violation. At the same time, people served by intermediate sized (500 to 100 000 people served) groundwater systems may be at higher risk for prolonged nitrate exposure (Figure 2c, SI File S9c). While short-term exposure to nitrate has some health risks, particularly for infants,[18] Ward et al.[17a,71] and others[72] found significant cancer and other health risks for long-term (>10 years) exposure to nitrate in drinking water. Since groundwater can take up to 60 years (particularly in deep oxic groundwater with long retention times) to return to natural background levels through natural flushing and recharge,[43a,b] treatment or remediation[73] may be required for smaller groundwater systems in violation, which may not have the option of switching water sources. Targeting CWSs with persistent nitrate problems for treatment upgrades or remediation may provide significant reductions in health risks.

The increase in the proportion of systems violating the nitrate MCL over time could have significant economic implications. For example, in 2005 when there was a nitrate drinking water advisory for systems in northern California and Nevada, the avoidance costs associated with purchasing bottled water were $60 million (a 26% increase in bottled water sales due to nitrate violations).[74] There are also increased treatment costs or source water protection costs associated with contaminated drinking water.[75] Ribaudo et al.[76] estimated that the nitrogen removal costs for individual CWSs can range from $19,500 to $815,000 per year, depending on the size of the water system. While it is difficult to accurately quantify the cost-benefits of treatment vs source water protection, one study in Ohio found the costs for source water protection to exceed the costs for treatment.[75] Other studies show that treatment can cost 30−40 times more than prevention,[77] and many utilities and local organization are making investments to protect their watersheds.[78] Also, there may be a great need for source water protection, as 78% of the land of the CONUS lies in a watershed that supplies drinking water, and this land is gradually becoming more urbanized and losing natural vegetation.[79]

Future work should investigate the cause of nitrate MCL violations, including associations between land use or N inputs, hydrogeologic factors, and when and where nitrate violations are most prevalent. This work may help inform management decisions aimed at minimizing public health risk. Future reductions in the number of violations and people served by systems in violation will require efforts to better treat contaminated source water and/or prevent further contamination of drinking water sources through source water protection measures.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

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Additional information as noted in the text (PDF)

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■ REFERENCES

(1) (a) Gleick, P. H. The human right to water. *Water policy* **1998**, *1* (5), 487−503. (b) Schwarzenbach, R. P.; Egli, T.; Hofstetter, T. B.; Von Gunten, U.; Wehrli, B. Global water pollution and human health. *Annual Review of Environment and Resources* **2010**, *35*, 109−136.

(2) Maupin, M. A.; Kenny, J. F.; Hutson, S. S.; Lovelace, J. K.; Barber, N. L.; Linsey, K. S. *Estimated use of water in the United States in 2010*; 2014; pp 56., https://pubs.usgs.gov/circ/1405.

(3) (a) Kreitler, C. W.; Jones, D. C. Natural soil nitrate: the cause of the nitrate contamination of ground water in Runnels County, Texas. *Groundwater* **1975**, *13* (1), 53−62. (b) Spalding, R. F.; Exner, M. E. Occurrence of nitrate in groundwater—a review. *J. Environ. Qual.* **1993**, *22* (3), 392−402. (c) Randall, G. W.; Mulla, D. J. Nitrate nitrogen in surface waters as influenced by climatic conditions and agricultural practices. *J. Environ. Qual.* **2001**, *30* (2), 337−344.

(4) (a) Hudak, P. Regional trends in nitrate content of Texas groundwater. *J. Hydrol.* **2000**, *228* (1), 37−47. (b) Glenn, S. M.; Lester, L. J. An analysis of the relationship between land use and arsenic, vanadium, nitrate and boron contamination in the Gulf Coast aquifer of Texas. *J. Hydrol.* **2010**, *389* (1), 214−226. (c) Mueller, D. K.; Hamilton, P. A.; Helsel, D. R.; Hitt, K. J.; Ruddy, B. C. *Nutrients in ground water and surface water of the United States—an analysis of data through 1992*; US Geological Survey Water-Resources Investigations Report 95−4031, 1995;. (d) Enwright, N.; Hudak, P. F. Spatial distribution of nitrate and related factors in the High Plains Aquifer, Texas. *Environ. Geol.* **2009**, *58* (7), 1541−1548. (e) Nolan, B. T.; Hitt, K. J.; Ruddy, B. C. Probability of nitrate contamination of recently

recharged groundwaters in the conterminous United States. *Environ. Sci. Technol.* **2002**, *36* (10), 2138−2145.

(5) Du, E.; de Vries, W.; Galloway, J. N.; Hu, X.; Fang, J. Changes in wet nitrogen deposition in the United States between 1985 and 2012. *Environ. Res. Lett.* **2014**, *9* (9), 095004.

(6) Pennino, M. J.; Kaushal, S. S.; Murthy, S. N.; Blomquist, J. D.; Cornwell, J. C.; Harris, L. A. Sources and transformations of anthropogenic nitrogen along an urban river-estuarine continuum. *Biogeosciences* **2016**, *13* (22), 6211.

(7) Meile, C.; Porubsky, W.; Walker, R.; Payne, K. Natural attenuation of nitrogen loading from septic effluents: Spatial and environmental controls. *Water Res.* **2010**, *44* (5), 1399−1408.

(8) (a) Pennino, M. J.; Kaushal, S. S.; Mayer, P. M.; Utz, R. M.; Cooper, C. A. Stream restoration and sewers impact sources and fluxes of water, carbon, and nutrients in urban watersheds. *Hydrol. Earth Syst. Sci.* **2016**, *20* (8), 3419. (b) Kaushal, S. S.; Groffman, P. M.; Band, L. E.; Elliott, E. M.; Shields, C. A.; Kendall, C. Tracking Nonpoint Source Nitrogen Pollution in Human-Impacted Watersheds. *Environ. Sci. Technol.* **2011**, *45* (19), 8225−8232.

(9) Taylor, G. D.; Fletcher, T. D.; Wong, T. H.; Breen, P. F.; Duncan, H. P. Nitrogen composition in urban runoff—implications for stormwater management. *Water Res.* **2005**, *39* (10), 1982−1989.

(10) Howarth, R. W.; Boyer, E. W.; Pabich, W. J.; Galloway, J. N. Nitrogen use in the United States from 1961−2000 and potential future trends. *Ambio* **2002**, *31* (2), 88−96.

(11) Sobota, D. J.; Compton, J. E.; Harrison, J. A. Reactive nitrogen inputs to US lands and waterways: how certain are we about sources and fluxes? *Frontiers in Ecology and the Environment* **2013**, *11* (2), 82−90.

(12) Eickhout, B.; Bouwman, A. F.; van Zeijts, H. The role of nitrogen in world food production and environmental sustainability. *Agric., Ecosyst. Environ.* **2006**, *116* (1−2), 4−14.

(13) (a) Vitousek, P. M.; Aber, J. D.; Howarth, R. W.; Likens, G. E.; Matson, P. A.; Schindler, D. W.; Schlesinger, W. H.; Tilman, D. Human alteration of the global nitrogen cycle: Sources and consequences. *Ecological Applications* **1997**, *7* (3), 737−750. (b) Driscoll, C. T.; Whitall, D.; Aber, J.; Boyer, E.; Castro, M.; Cronan, C.; Goodale, C. L.; Groffman, P.; Hopkinson, C.; Lambert, K.; Lawrence, G.; Ollinger, S. Nitrogen pollution in the northeastern United States: Sources, effects, and management options. *BioScience* **2003**, *53* (4), 357−374.

(14) (a) Boesch, D. F.; Brinsfield, R. B.; Magnien, R. E. Chesapeake Bay eutrophication: Scientific understanding, ecosystem restoration, and challenges for agriculture. *J. Environ. Qual.* **2001**, *30* (2), 303−320. (b) Diaz, R. J. Overview of hypoxia around the world. *J. Environ. Qual.* **2001**, *30* (2), 275−281.

(15) Townsend, A. R.; Howarth, R. W.; Bazzaz, F. A.; Booth, M. S.; Cleveland, C. C.; Collinge, S. K.; Dobson, A. P.; Epstein, P. R.; Keeney, D. R.; Mallin, M. A.; Rogers, C. A.; Wayne, P.; Wolfe, A. H. Human health effects of a changing global nitrogen cycle. *Frontiers in Ecology and the Environment* **2003**, *1* (5), 240−246.

(16) Ward, M. H.; DeKok, T. M.; Levallois, P.; Brender, J.; Gulis, G.; Nolan, B. T.; VanDerslice, J. Workgroup report: Drinking-water nitrate and health-recent findings and research needs. *Environ. Health Perspect.* **2005**, *113*, 1607−1614.

(17) (a) Ward, M. H.; Kilfoy, B. A.; Weyer, P. J.; Anderson, K. E.; AFolsom, A. R.; Cerhan, J. R. Nitrate intake and the risk of thyroid cancer and thyroid disease. *Epidemiology (Cambridge, Mass.)* **2010**, *21* (3), 389. (b) Weyer, P. J.; Cerhan, J. R.; Kross, B. C.; Hallberg, G. R.; Kantamneni, J.; Breuer, G.; Jones, M. P.; Zheng, W.; Lynch, C. F. Municipal drinking water nitrate level and cancer risk in older women: the Iowa Women's Health Study. *Epidemiology* **2001**, *12* (3), 327−338. (c) Jones, R. R.; Weyer, P. J.; Dellavalle, C. T.; Inoue-Choi, M.; Anderson, K. E.; Cantor, K. P.; Krasner, S.; Robien, K.; Beane Freeman, L. E.; Silverman, D. T., Nitrate from Drinking Water and Diet and Bladder Cancer among Postmenopausal Women in Iowa. *Environ. Health Perspect.* **2016**;.10.1289/EHP191 (d) Inoue-Choi, M.; Jones, R. R.; Anderson, K. E.; Cantor, K. P.; Cerhan, J. R.; Krasner, S.; Robien, K.; Weyer, P. J.; Ward, M. H. Nitrate and nitrite ingestion and risk of ovarian cancer among postmenopausal women in Iowa. *Int. J. Cancer* **2015**, *137* (1), 173−182. (e) De Roos, A. J.; Ward, M. H.; Lynch, C. F.; Cantor, K. P. Nitrate in public water supplies and the risk of colon and rectum cancers. *Epidemiology* **2003**, *14* (6), 640−649.

(18) Brender, J. D.; Weyer, P. J.; Romitti, P. A.; Mohanty, B. P.; Shinde, M. U.; Vuong, A. M.; Sharkey, J. R.; Dwivedi, D.; Horel, S. A.; Kantamneni, J. Prenatal nitrate intake from drinking water and selected birth defects in offspring of participants in the National Birth Defects Prevention Study. *Environ. Health Perspect.* **2013**, *121* (9), 1083.

(19) (a) Coss, A.; Cantor, K. P.; Reif, J. S.; Lynch, C. F.; Ward, M. H. Pancreatic cancer and drinking water and dietary sources of nitrate and nitrite. *Am. J. Epidemiol.* **2004**, *159* (7), 693−701. (b) Arbuckle, T. E.; Sherman, G. J.; Corey, P. N.; Walters, D.; Lo, B. Water nitrates and CNS birth defects: a population-based case-control study. *Arch. Environ. Health* **1988**, *43* (2), 162−167.

(20) (a) U.S. EPA Drinking Water Requirements for States and Public Water Systems: Information about Public Water Systems. https://www.epa.gov/dwreginfo/information-about-public-water-systems (accessed February 15, 2017);. (b) CFR Code of Federal Regulations. Title 40 - Protection of the Environment, Chapter I, Subchapter D, Part 141 - National Primary Drinking Water Regulations, Subpart A-General, Section 141.2 Definitions. https://www.ecfr.gov/cgi-bin/text-idx?SID=276258188c64033cb302c0d165c57c7f&mc=true&node=pt40.25.141&rgn=div5#se40.25.141_12 (accessed May 23, 2017).

(21) U.S. EPA. United States Environment Protection Agency. Factoids: Drinking Water and Groundwater Statistics for 2008. Available online: http://www.circleofblue.org/wp-content/uploads/2010/11/EPA-water-data-2008.pdf *(Accessed on 22 November 2016)*; 2008.

(22) SDWIS. U.S. Environmental Protection Agency Safe Drinking Water Information System. https://ofmpub.epa.gov/apex/sfdw/f?p=108:1:::NO:1 (accessed September 15, 2016).

(23) U.S. EPA Information about Public Water Systems. https://www.epa.gov/dwreginfo/information-about-public-water-systems (accessed October 28).

(24) CFR *Code of Federal Regulations. Inorganic chemical sampling and analytical requirements. Title 40 - Protection of the Environment, Chapter I, Subchapter D, Part 141, Subpart C, Section 141.23*; 2016.

(25) CFR, Code of Federal Regulations. Inorganic chemical sampling and analytical requirements. Title 40 - Protection of the Environment, Chapter I, Subchapter D, Part 141, Subpart C, Section 141.23. 1986.

(26) R Development Core Team R: A Language and Environment for Statistical Computing. http://www.R-project.org.

(27) Fedinick, K. P.; Wu, M.; Mekela Panditharatne, J. *Threats on tap: Widespread violations highlight need for investment in water infrastructure and protections*; Natural Resource Defense Council R: 17-02-A, 2017.

(28) Nolan, B. T.; Hitt, K. J. Vulnerability of shallow groundwater and drinking-water wells to nitrate in the United States. *Environ. Sci. Technol.* **2006**, *40* (24), 7834−7840.

(29) Community for Data Integration, County-level "Land drained by tile" (and other land use practices) from the 2012 Census of Agriculture U.S. Geological Survey. https://my.usgs.gov/confluence/display/cdi/ETWG+Integration+-+Tile+drainage: 2016.

(30) Homer, C.; Dewitz, J.; Yang, L.; Jin, S.; Danielson, P.; Xian, G.; Coulston, J.; Herold, N.; Wickham, J.; Megown, K. Completion of the 2011 National Land Cover Database for the conterminous United States—representing a decade of land cover change information. *Photogrammetric Engineering & Remote Sensing* **2015**, *81* (5), 345−354.

(31) Soil Survey Staff. Natural Resources Conservation Service. United States Department of Agriculture. Web Soil Survey. Available online at http://websoilsurvey.nrcs.usda.gov/ (accessed October 4, 2017).

(32) Daly, C.; Halbleib, M.; Smith, J. I.; Gibson, W. P.; Doggett, M. K.; Taylor, G. H.; Curtis, J.; Pasteris, P. P. Physiographically sensitive mapping of climatological temperature and precipitation across the conterminous United States. *International journal of climatology* **2008**, *28* (15), 2031−2064.

(33) USGS. Spatial Data Sets Available on the WRD NSDI Node. U.S. Geological Survey. https://water.usgs.gov/lookup/getgislist (accessed October 4, 2017).

(34) Rupert, M. G. Decadal-scale changes of nitrate in ground water of the United States, 1988–2004. *J. Environ. Qual.* **2008**, *37* (5_Supplement), S-240–S-248.

(35) Lindsey, B. D.; Rupert, M. G. *Methods for Evaluating Temporal Groundwater Quality Data and Results of Decadal-Scale Changes in Chloride, Dissolved Solids, and Nitrate Concentrations in Groundwater in the United States, 1988–2010*; U.S. Geological Survey Scientific Investigations Report 2012–5049, 2012; pp 46., https://pubs.usgs.gov/sir/2012/5049/.

(36) Burow, K. R.; Jurgens, B. C.; Belitz, K.; Dubrovsky, N. M. Assessment of regional change in nitrate concentrations in groundwater in the Central Valley, California, USA, 1950s-2000s. *Environ. Earth Sci.* **2013**, *69* (8), 2609–2621.

(37) Chaudhuri, S.; Ale, S. Long term (1960–2010) trends in groundwater contamination and salinization in the Ogallala aquifer in Texas. *J. Hydrol.* **2014**, *513*, 376–390.

(38) (a) Dubrovsky, N. M.; Burow, K. R.; Clark, G. M.; Gronberg, J.; Hamilton, P. A.; Hitt, K. J.; Mueller, D. K.; Munn, M. D.; Nolan, B. T.; Puckett, L. J. *The Quality of Our Nation's Waters-Nutrients in the Nation'S Streams and Groundwater, 1992–2004*; US Geological Survey Circular *1350*, 2010;. (b) Della Rocca, C.; Belgiorno, V.; Meriç, S. Overview of in-situ applicable nitrate removal processes. *Desalination* **2007**, *204* (1–3), 46–62.

(39) (a) Fenn, M. E.; Haeuber, R.; Tonnesen, G. S.; Baron, J. S.; Grossman-Clarke, S.; Hope, D.; Jaffe, D. A.; Copeland, S.; Geiser, L.; Rueth, H. M. Nitrogen emissions, deposition, and monitoring in the western United States. *BioScience* **2003**, *53* (4), 391–403. (b) Gronberg, J. A. M.; Spahr, N. E. *County-Level Estimates of Nitrogen and Phosphorus from Commercial Fertilizer for the Conterminous United States, 1987–2006*; US Geological Survey Report 2012–5207, 2012;. (c) Compton, J. E.; Harrison, J. A.; Dennis, R. L.; Greaver, T. L.; Hill, B. H.; Jordan, S. J.; Walker, H.; Campbell, H. V. Ecosystem services altered by human changes in the nitrogen cycle: a new perspective for US decision making. *Ecology Letters* **2011**, *14* (8), 804–815.

(40) (a) Thornton, P. K. Livestock production: recent trends, future prospects. *Philos. Trans. R. Soc., B* **2010**, *365* (1554), 2853–2867. (b) Nierenberg, D.; Reynolds, L. Farm Animal Populations Continue to Grow. http://vitalsigns.worldwatch.org/vs-trend/farm-animal-populations-continue-grow (accessed April 27, 2017).

(41) U.S. EPA Nitrogen Oxides (NOx) Control Regulations. https://www3.epa.gov/region1/airquality/nox.html (accessed February 24, 2017).

(42) Li, Y.; Schichtel, B. A.; Walker, J. T.; Schwede, D. B.; Chen, X.; Lehmann, C. M.; Puchalski, M. A.; Gay, D. A.; Collett, J. L. Increasing importance of deposition of reduced nitrogen in the United States. *Proc. Natl. Acad. Sci. U. S. A.* **2016**, *113*, 201525736.

(43) (a) Katz, B.; Berndt, M.; Crandall, C. Factors affecting the movement and persistence of nitrate and pesticides in the surficial and upper Floridan aquifers in two agricultural areas in the southeastern United States. *Environ. Earth Sci.* **2014**, *71* (6), 2779–2795. (b) Repert, D. A.; Barber, L. B.; Hess, K. M.; Keefe, S. H.; Kent, D. B.; LeBlanc, D. R.; Smith, R. L. Long-term natural attenuation of carbon and nitrogen within a groundwater plume after removal of the treated wastewater source. *Environ. Sci. Technol.* **2006**, *40* (4), 1154–1162. (c) Kim, J. J.; Comstock, J.; Ryan, P.; Heindel, C.; Koenigsberger, S. Denitrification and dilution along fracture flowpaths influence the recovery of a bedrock aquifer from nitrate contamination. *Sci. Total Environ.* **2016**, *569*, 450–468. (d) Puckett, L. J.; Tesoriero, A. J.; Dubrovsky, N. M. Nitrogen Contamination of Surficial Aquifers - A Growing Legacy. *Environ. Sci. Technol.* **2011**, *45* (3), 839–844.

(44) Dwivedi, D.; Mohanty, B. P. Hot spots and persistence of nitrate in aquifers across scales. *Entropy* **2016**, *18* (1), 25.

(45) (a) Mastrocicco, M.; Colombani, N.; Castaldelli, G.; Jovanovic, N. Monitoring and modeling nitrate persistence in a shallow aquifer. *Water, Air, Soil Pollut.* **2011**, *217* (1–4), 83–93. (b) Exner, M. E.; Hirsh, A. J.; Spalding, R. F. Nebraska's groundwater legacy: Nitrate contamination beneath irrigated cropland. *Water Resour. Res.* **2014**, *50* (5), 4474–4489.

(46) Lassaletta, L.; Billen, G.; Grizzetti, B.; Anglade, J.; Garnier, J. 50 year trends in nitrogen use efficiency of world cropping systems: the relationship between yield and nitrogen input to cropland. *Environ. Res. Lett.* **2014**, *9* (10), 105011.

(47) USDA Fertilizer Use and Price. https://www.ers.usda.gov/data-products/fertilizer-use-and-price (accessed February 27, 2017).

(48) Wang, X.; Wang, J. Removal of nitrate from groundwater by heterotrophic denitrification using the solid carbon source. *Sci. China, Ser. B: Chem.* **2009**, *52* (2), 236–240.

(49) Sun, S.; Sun, G.; Caldwell, P.; McNulty, S.; Cohen, E.; Xiao, J.; Zhang, Y. Drought impacts on ecosystem functions of the US National Forests and Grasslands: Part II assessment results and management implications. *For. Ecol. Manage.* **2015**, *353*, 269–279.

(50) (a) Cevaal, J. N.; Suratt, W. B.; Burke, J. E. Nitrate removal and water quality improvements with reverse osmosis for Brighton, Colorado. *Desalination* **1995**, *103* (1), 101–111. (b) Des Moines Water Works Water Treatment Process. http://www.dmww.com/water-quality/treatment-process/ (accessed March 3, 2017).

(51) (a) Kapoor, A.; Viraraghavan, T. Nitrate removal from drinking water—review. *J. Environ. Eng.* **1997**, *123* (4), 371–380. (b) Jacangelo, J. G.; Trussell, R. R.; Watson, M. Role of membrane technology in drinking water treatment in the United States. *Desalination* **1997**, *113* (2–3), 119–127.

(52) (a) City of Columbus Elevated Nitrate Levels: Nitrate in Drinking Water. https://www.columbus.gov/utilities/water-protection/wqal/Elevated-Nitrate-Levels/ (accessed February 27, 2017);. (b) Columbus Dispatch Columbus saw nitrate problem coming down Scioto River. http://www.dispatch.com/content/stories/local/2015/06/10/city-saw-nitrate-problem-coming-down-the-river.html (accessed February 27, 2017).

(53) City of Columbus Nitrate Advisory. https://www.columbus.gov/nitrate_food_advisory/ (accessed February 27, 2017).

(54) Ohio Revised Code Ohio Revised Code. Title IX Agriculture, Animals, Fences. Chapter 905: AGRICULTURAL ADDITIVES AND LIME; FERTILIZER. 905.326 Application of fertilizer in western basin. http://codes.ohio.gov/orc/905.

(55) (a) Munster, J. E. Evaluating nitrate sources in Suffolk County groundwater, Stony Brook University. Long Island, NY, 2004;. (b) Koch, F.; Cary, S.; Szabo, J. W.; Dawydiak, W.; Irwin, D.; Schneider, B.; Dale, D.; Ostuni, C.; White, M. *State of the Aquifer 2016*; Long Island Comission for Aquifer Protection, 2016.

(56) (a) Burkart, M. R.; Kolpin, D. W. Hydrologic and land-use factors associated with herbicides and nitrate in near-surface aquifers. *J. Environ. Qual.* **1993**, *22* (4), 646–656. (b) Hudak, P. F. Solute distribution in the Ogallala Aquifer, Texas: lithium, fluoride, nitrate, chloride and bromide. *Carbonates Evaporites* **2016**, *31* (4), 437–448.

(57) (a) Richards, R. P.; Baker, D. B.; Creamer, N. L.; Kramer, J. W.; Ewing, D. E.; Merryfield, B. J.; Wallrabenstein, L. K. Well water quality, well vulnerability, and agricultural contamination in the Midwestern United States. *J. Environ. Qual.* **1996**, *25* (3), 389–402. (b) Rivett, M. O.; Buss, S. R.; Morgan, P.; Smith, J. W.; Bemment, C. D. Nitrate attenuation in groundwater: a review of biogeochemical controlling processes. *Water Res.* **2008**, *42* (16), 4215–4232.

(58) (a) Ruddy, B. C.; Lorenz, D. L.; Mueller, D. K. *County-level estimates of nutrient inputs to the landsurface of the conterminous United States, 1982–2001*; 2328–0328; US Geological Survey: 2006;. (b) U.S. EPA Commercial Fertilizer Purchased. https://www.epa.gov/nutrient-policy-data/commercial-fertilizer-purchased (accessed February 28, 2017).

(59) (a) Resilience.org Kansas Town Faces Big Bill to Clean Drinking Water. http://www.resilience.org/stories/2017-01-25/kansas-town-faces-big-bill-to-clean-drinking-water/ (accessed February 27, 2017);. (b) NET Watching Our Water: How are nitrates ending up in drinking water supplies? http://netnebraska.org/article/news/1042068/watching-our-water-how-are-nitrates-ending-drinking-water-supplies (accessed February 28, 2017).

(60) (a) Carey, B.; Cummings, R. *Sumas-Blaine Aquifer Nitrate Contamination Summary*; Washington State Department of Ecology, Olympia, WA.,Publication No. 12−03−026. www.ecy.wa.gov/biblio/1203026.htm, 2012;. (b) Almasri, M. N.; Kaluarachchi, J. J. Assessment and management of long-term nitrate pollution of ground water in agriculture-dominated watersheds. *J. Hydrol.* **2004**, *295* (1), 225−245.

(61) Lockhart, K.; King, A.; Harter, T. Identifying sources of groundwater nitrate contamination in a large alluvial groundwater basin with highly diversified intensive agricultural production. *J. Contam. Hydrol.* **2013**, *151*, 140−154.

(62) U.S. EPA Estimated Nitrate Concentrations in Groundwater Used for Drinking. https://www.epa.gov/nutrient-policy-data/estimated-nitrate-concentrations-groundwater-used-drinking (accessed February 28, 2017).

(63) Nolan, B. T.; Ruddy, B. C.; Hitt, K. J.; Helsel, D. R. Risk of Nitrate in groundwaters of the United States a national perspective. *Environ. Sci. Technol.* **1997**, *31* (8), 2229−2236.

(64) Burow, K. R.; Nolan, B. T.; Rupert, M. G.; Dubrovsky, N. M. Nitrate in groundwater of the United States, 1991− 2003. *Environ. Sci. Technol.* **2010**, *44* (13), 4988−4997.

(65) Moody, D. W. Groundwater contamination in the United States. *Journal of Soil and Water Conservation* **1990**, *45* (2), 170−179.

(66) U.S. EPA Percentage of Surface Drinking Water from Intermittent, Ephemeral, and Headwater Streams. https://www.epa.gov/cwa-404/geographic-information-systems-analysis-surface-drinking-water-provided-intermittent (accessed March 1, 2017).

(67) (a) Carpenter, S. R.; Caraco, N. F.; Correll, D. L.; Howarth, R. W.; Sharpley, A. N.; Smith, V. H. Nonpoint pollution of surface waters with phosphorus and nitrogen. *Ecological Applications* **1998**, *8* (3), 559−568. (b) Kalita, P.; Cooke, R.; Anderson, S.; Hirschi, M.; Mitchell, J. Subsurface drainage and water quality: The Illinois experience. *Trans. ASABE* **2007**, *50* (5), 1651−1656.

(68) Petry, J.; Soulsby, C.; Malcolm, I.; Youngson, A. Hydrological controls on nutrient concentrations and fluxes in agricultural catchments. *Sci. Total Environ.* **2002**, *294* (1), 95−110.

(69) Mander, Ü.; Kull, A.; Kuusemets, V.; Tamm, T. Nutrient runoff dynamics in a rural catchment: influence of land-use changes, climatic fluctuations and ecotechnological measures. *Ecological Engineering* **2000**, *14* (4), 405−417.

(70) Beauvais, J., Renewed Call to Action to Reduce Nutrient Pollution and Support for Incremental Actions to Protect Water Quality and Public Health. State Environmental Commissioners, S. W. D., Ed. U.S. Environmental Protection Agency: Washginton, D.C., 2016; p 6.

(71) Ward, M. H.; Mark, S. D.; Cantor, K. P.; Weisenburger, D. D.; Correa-Villasenor, A.; Zahm, S. H. Drinking water nitrate and the risk of non-Hodgkin's lymphoma. *Epidemiology* **1996**, *7* (5), 465−471.

(72) Jones, R. R.; Weyer, P. J.; Dellavalle, C. T.; Inoue-Choi, M.; Anderson, K. E.; Cantor, K. P.; Krasner, S.; Robien, K.; Freeman, L. E. B.; Silverman, D. T. Nitrate from drinking water and diet and bladder cancer among postmenopausal women in Iowa. *Environ. Health Perspect.* **2016**, *124* (11), 1751.

(73) (a) Thiruvenkatachari, R.; Vigneswaran, S.; Naidu, R. Permeable reactive barrier for groundwater remediation. *J. Ind. Eng. Chem.* **2008**, *14* (2), 145−156. (b) Fu, F.; Dionysiou, D. D.; Liu, H. The use of zero-valent iron for groundwater remediation and wastewater treatment: a review. *J. Hazard. Mater.* **2014**, *267*, 194−205.

(74) Zivin, J. G.; Neidell, M.; Schlenker, W. Water quality violations and avoidance behavior: Evidence from bottled water consumption. *American Economic Review* **2011**, *101* (3), 448−453.

(75) Heberling, M. T.; Nietch, C. T.; Thurston, H. W.; Elovitz, M.; Birkenhauer, K. H.; Panguluri, S.; Ramakrishnan, B.; Heiser, E.; Neyer, T. Comparing drinking water treatment costs to source water protection costs using time series analysis. *Water Resour. Res.* **2015**, *51* (11), 8741−8756.

(76) Ribaudo, M.; Hansen, L.; Livingston, M.; Mosheim, R.; Williamson, J.; Delgado, J., Nitrogen in agricultural systems: Implications for conservation policy. *USDA-ERS Economic Research Report* 2011, (127).

(77) U.S. EPA *Benefits and Costs of Prevention: Case Studies of Community Wellhead Protection. Volume 1*; EPA 813-B-95-005. http://nepis.epa.gov/Exe/ZyPDF.cgi?Dockey=20001U4L.PDF, 1996.

(78) (a) Bennett, D. E.; Gosnell, H.; Lurie, S.; Duncan, S. Utility engagement with payments for watershed services in the United States. *Ecosystem Services* **2014**, *8*, 56−64. (b) Gartner, E. T.; Mulligan, J.; Schmidt, R.; Gunn, J., Natural Infrastructure Investing in Forested Landscapes for Source Water Protection in the United States. 2013.

(79) Wickham, J. D.; Wade, T. G.; Riitters, K. H. An environmental assessment of United States drinking water watersheds. *Landscape Ecology* **2011**, *26* (5), 605.