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Article

# Landscape Drivers of Dynamic Change in Water Quality of U.S. Rivers

Edward G. Stets,* Lori A. Sprague, Gretchen P. Oelsner, Hank M. Johnson, Jennifer C. Murphy, Karen Ryberg, Aldo V. Vecchia, Robert E. Zuellig, James A. Falcone, and Melissa L. Riskin

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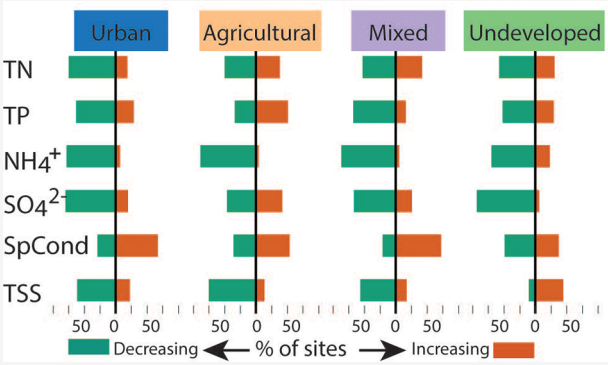
**ABSTRACT:** Water security is a top concern for social well-being, and dramatic changes in the availability of freshwater have occurred as a result of human uses and landscape management. Elevated nutrient loading and perturbations to major ion composition have resulted from human activities and have degraded freshwater resources. This study addresses the emerging nature of streamwater quality in the 21st century through analysis of concentrations and trends in a wide variety of constituents in streams and rivers of the U.S. Concentrations of 15 water quality constituents including nutrients, major ions, sediment, and specific conductance were analyzed over the period 1982−2012 and a targeted trend analysis was performed from 1992 to 2012. Although environmental policy is geared toward addressing the long-standing problem of nutrient overenrichment, these efforts have had uneven success, with decreasing nutrient concentrations at urbanized sites and little to no change at agricultural sites. Additionally, freshwaters are being salinized rapidly in all human-dominated land use types. While efforts to control nutrients are ongoing, rapid salinity increases are ushering in a new set of poorly defined issues. Increasing salinity negatively affects biodiversity, mobilizes sediment-bound contaminants, and increases lead contamination of drinking water, but its effects are not well integrated into current paradigms of water management.




## INTRODUCTION

Freshwater resources are critical to human health, economic vitality, and ecosystem integrity. The World Economic Forum rates water security as one of the top concerns for social well-being,[1] and water shortages are a source of conflict worldwide.[2] Global observations confirm that human use and climate change are driving dynamic changes in water availability[3] and pollution is a major cause of water insecurity.[4]

Major efforts to mitigate the degradation of water quality have been implemented in the U.S. For example, the Clean Water Act focused on upgrading wastewater treatment plants (WWTPs) to decrease point discharges of nutrients and organic material.[5] Best management practices have been implemented in some locations to address nonpoint source pollution arising from agricultural land use.[6,7] Controls on sulfur and nitrogen emissions have decreased acid precipitation and resulted in measurable changes in water quality.[8,9] But despite the successes of these efforts, some areas of the U.S. have experienced continued or worsening water quality. Elevated nutrient concentrations and loads have been observed in headwaters, rivers, and downstream receiving waters[10−12] resulting in reduced biodiversity, harmful algal blooms, hypoxic zones, and compromised water quality for human uses.[4,9,11,12] More recently, a widespread increase in salinity has been identified.[13] Elevated salinity can have various effects on aquatic ecosystems and water availability including increased mobilization of metals and other pollutants, decreased organic matter decomposition, and losses of biodiversity.[13−15] Elevated salinity can also affect human health and infrastructure by promoting corrosion, which can be costly to repair and is linked to increased metal contamination of drinking water.[16,17]

The large changes in water quality experienced in the U.S. and elsewhere are often strongly related to land use[18] for two reasons. First, terrestrial environments are source areas for the solutes, sediments, and physical characteristics that determine water quality. Second, environmental policy and management often attempt to target activities occurring in specific land use types, and so there should be commonalities in how water quality responds to these management actions. Agricultural and urbanized land uses broadly encompass contrasting anthropogenic activities and are typically the focus of

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management measures aimed at mitigating water pollution. Studies on water quality trends often target specific water quality constituents, specific regions, or sites in a particular land use[10,19,20] while national, comprehensive analyses of water quality trends are much less common. As a result, our overall perspective on water quality problems is more limited at the national scale despite the large amount of resources dedicated to water quality improvements in urban and agricultural landscapes. Here we analyze trends in water quality in streams and rivers of the conterminous U.S. This study was conducted to gain insight into changes in the concentrations of multiple water quality constituents in various land use types throughout the conterminous U.S. We looked at multidecadal trends for 15 water quality constituents and interpreted the trends based upon broad characterizations of watershed land use. Considering the changes in many constituents over a long time period provided a framework for understanding how water quality has changed in different land use types and provided important insights into the ongoing evolution of surface water quality in the conterminous U.S.

## ■ MATERIALS AND METHODS

**Data Sources.** Water quality data were acquired from national, state, and local sources. The goal was to compile the most comprehensive data set possible to assess the status and trends of water quality of rivers in the conterminous U.S. This goal was achieved through a long process of data vetting, harmonization, checking, and quality assurance/quality control. The challenges associated with using data from multiple agencies for trend analysis limited our ability to adequately assess changes in water quality in a timely manner and a significant amount of monitoring data was left out of the study because it was not suitable for assimilation into a national-scale assessment.[21] Nevertheless, the information presented here provides important insights into the patterns of change in U.S. water quality over the past several decades.

Data obtained from the assimilation effort were matched with stream discharge records and used to run the Watershed Regressions on Time, Discharge, and Season (WRTDS) model.[22] WRTDS output was used to produce annual flow-normalized concentration for all water quality constituents and to perform trend analysis. Sites were assessed for data coverage during the time periods 1982−2012 and 1992−2012. Trend analysis was limited to the time period 1992−2012 because the larger number of sites allowed comparisons of the distributions of trends across land use types. Trend analysis was performed for the period 1992−2012 using likelihood analysis of differences in bootstrapped annual concentrations between the beginning and ending years.[23] Fewer sites passed data screens for inclusion in the analysis beginning in 1982, but these sites add valuable perspective on longer-term changes in water quality, so they were added for use in the estimated marginal means (EMM) analysis, explained below.

Trend in concentration was the primary response variable considered and was expressed in units of mg $L^{-1}$ for most constituents and $\mu$mhos $cm^{-1}$ for specific conductance (SpCond). We categorized water quality constituents as nutrients, major ions, or sediment. Nutrients included total nitrogen (TN), nitrate ($NO_3^-$), ammonium ($NH_4^+$), total phosphorus (TP), soluble reactive phosphorus (SRP), and total organic carbon (TOC). Major ions included calcium ($Ca^{2+}$), magnesium ($Mg^{2+}$), sodium ($Na^+$), potassium ($K^+$), alkalinity (measured as total alkalinity and expressed as mg $L^{-1}$ $CaCO_3$), sulfate ($SO_4^{2-}$), and chloride ($Cl^-$). SpCond, which is often used as a surrogate for total dissolved solids or salinity, was included in the *major ions* category. Sediment was measured as total suspended solids (TSS).

Streamflow data, which were required for WRTDS model runs, originated primarily from the U.S. Geological Survey (USGS) streamgage network and were obtained from the USGS National Water Information System database (NWIS).[24] Out of 633 total sites used in this analysis, streamflow data were obtained from the USGS for 626 sites and other agencies for 7 sites. In most cases, the water quality and stream discharge data originated from the same location. Otherwise, water quality and stream discharge data were matched using the National Hydrography Data set (NHDPlus V2Medium Resolution data set).[25] An indexing algorithm was used to match monitoring stations on streamflow lines in NHDPlus and then to locate nearby streamgage stations. Water quality monitoring stations were matched to gaging stations if the reported drainage basin area of each was within 10% and if basic metrics of data coverage were met by the gaging station. More detailed descriptions of the gage matching routines are are reported elsewhere.[26]

**Trend Analysis.** Trend detection was performed using WRTDS implemented using the R programming language packages *EGRET* and *EGRETci*.[27,28] Trends were quantified as differences in the bootstrapped flow-normalized concentration estimates between the beginning and ending years ($y_S$ and $y_E$, respectively). Each bootstrap replicate created an estimate of annual flow-normalized concentration in all years including $y_S$ and $y_E$. The difference in concentration between $y_S$ and $y_E$ ($\Delta C$) could be either positive or negative. For each site-constituent combination, 100 bootstrap replicates were created. More detail on the bootstrapping method is given in ref 23. Hypothesis testing was implemented using likelihood analysis with the proportion of bootstrap estimates with $\Delta C > 0$ and $\Delta C < 0$ used to generate likelihood estimates. Models with >70% likelihood of either a positive or negative trend were considered to have some evidence that a trend exists for the given site-constituent combination.

**Land Use.** Land use was categorized using the Wall-to-Wall Anthropogenic Land Use Trends (NWALT) data set for 2012.[29] Watersheds were categorized as either undeveloped, agricultural, urban, or mixed land use based on percent coverage of the watershed of NWALT classes for the year 2012 (Supporting Information (SI) Table S1).

**Estimated Marginal Means.** To provide insight into the timing and magnitude of changes, the annual estimated marginal means (EMM) of constituent concentration were calculated and reported. EMM provides an estimate of mean constituent concentration across all sites included in the analysis for each year of the study. A similar approach using least-squares means has been used elsewhere.[30] EMM was used because of the unbalanced structure of the data. That is, each year included a different number of sites and so a bias could be introduced if the simple means across sites were used for each year. EMM was used for visualization purposes and was not used to detect trends. EMM were calculated using the package *emmeans* version 1.3.2 in R 3.4.3.[31]

EMM were based on a two-factor ANOVA for each constituent:

$$\ln Y = \text{site} + \text{year} + \varepsilon$$


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where $Y$ is the constituent concentration, site is a categorical variable representing each monitoring station, year is a categorical variable for any year between 1982 and 2012, and $\varepsilon$ is the residual error of the model. An example showing the EMM of TP along with results from all sites is shown in SI Figure S2. The response variable, $Y$, was natural log-transformed to ensure normality. The model was run separately for each constituent and land use category. In a few instances, the model was not significant when the year term was not significant. This outcome corresponded to constituent-land use combinations with very little change in concentration over time. The model sometimes produced discontinuities in cases where large numbers of sites entered the analysis on the same year based on the way we screened sites.

## RESULTS AND DISCUSSION

**Nutrients.** Dramatic changes in the water quality of U.S. streams and rivers were evident in our analysis and point to an important evolution in water quality in U.S. rivers. The use of EMM and central tendencies of trends between 1992 and 2012 allowed generalizations about the behavior of different land use types, but de-emphasized site-specific differences within the data set. Therefore, interpretations should be viewed as the aggregate behavior of sites within broad land use categories with the likelihood that individual sites or areas are behaving in ways that are different than the aggregate. Nevertheless, important patterns emerged when grouping the sites in this way.

Undeveloped sites had the lowest concentrations for all nutrients throughout the period of analysis (Figure 1). Agricultural sites had the highest concentrations of TN, $NO_3^-$, and TOC, ~ 2.2, 1.4, and 6.3 mg $L^{-1}$, respectively (Figure 1). TP concentration was initially highest at urban sites, ~ 0.3 mg $L^{-1}$, but decreased through time such that agricultural areas had the highest TP concentrations, ~ 0.2 mg $L^{-1}$, by 1991 (Figure 1). Although the EMM analysis does not provide a rigorous statistical test for trends in concentrations, some trends were readily visible. Sites draining all land uses consistently show decreases in $NH_4^+$, urban watersheds show decreases in TN, TP, and TOC concentrations, and mixed land-use watersheds show decreases in SRP.

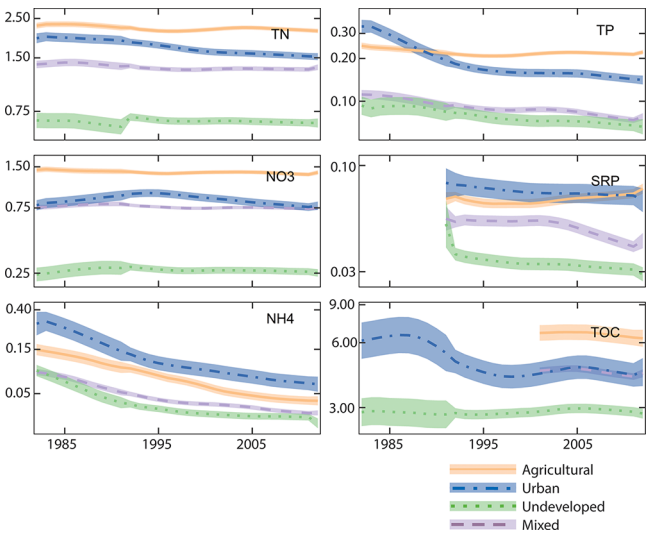


**Figure 1.** Estimated marginal mean of nutrients for every year 1982–2012 categorized by land use type. Units are elemental mg $L^{-1}$ for all constituents. Shaded areas show 95% confidence intervals around the estimated concentration. TN, total nitrogen; $NO_3$, nitrate; $NH_4$, ammonium; TP, total phosphorus; SRP, soluble reactive phosphorus; TOC, total organic carbon. Note that the $y$-axis is on a log scale.

The median of $\Delta C$, when calculated across all sites included in the analysis, was negative for all nutrient constituents. $\Delta C$ was quantified over the period 1992–2012 and summarized statistically in SI Tables S2–S4. Decreasing trends were particularly strong for $NH_4^+$, for which likely decreases were detected at 80% of sites (Figure 2, SI Table S2). For other constituents, trends varied by land use. For most constituents, decreasing trends were common at urban sites with $NO_3^-$ and TP decreasing at >60% of urban sites and $NH_4^+$, SRP, TN, and TOC decreasing at >70% of urban sites (Figure 2, SI Table S3). In contrast, only $NH_4^+$ and TOC were likely decreasing at more than half of agricultural sites and TP and SRP were likely increasing at more than half of sites (Figure 2, SI Table S3). TN and $NO_3$ were found to be likely decreasing at 50 and 40% of agricultural sites, respectively (Figure 2, SI Table S3). SRP, for which the record is shorter (Figure 1), decreased most strongly at mixed land use types and TOC increased in undeveloped areas (Figure 2).

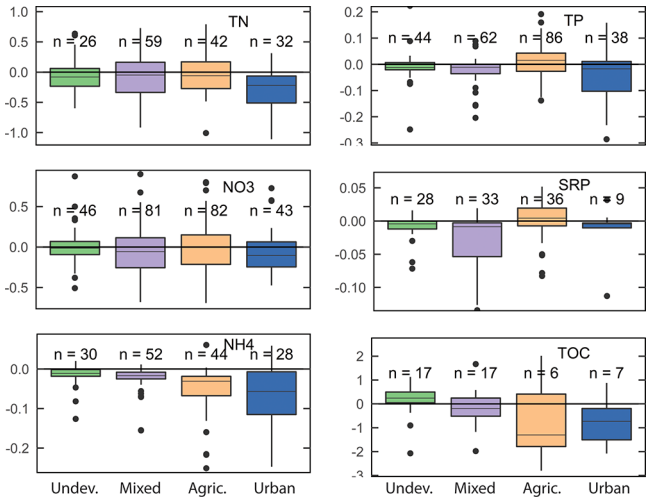


**Figure 2.** Boxplots of the change in concentration (1992–2012) of nutrients. Units are elemental mg $L^{-1}$ for all constituents. Values below 0 represent decreases and values above 0 represent increases. TN, total nitrogen; $NO_3$, nitrate; $NH_4$, ammonium; TP, total phosphorus; SRP, soluble reactive phosphoru; TOC, total organic carbon.

The decreasing nutrient concentrations observed at many of the urban sites included in this study (Figure 2, SI Table S3) indicate that management efforts in these areas have had some success. The 1972 Clean Water Act (CWA) focused heavily on the regulation of point discharges and the 1987 CWA reauthorization added important provisions for stormwater management. It is reasonable to expect that both of these sources of nutrients would be most important in urban areas. Therefore, the reduction in nutrients commonly observed in urban areas is likely to be due to the relative success of these efforts,[5,32] resulting in downward trends in nutrient concentrations in urban areas at the national scale.

The lack of widespread nutrient reductions at agricultural sites, despite the widely acknowledged role they play as nutrient sources to receiving waters, has been reported


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elsewhere.[11,33] The crucial question is whether nutrient reductions in these areas are simply not large enough nor widespread enough to result in downward trends or whether legacy nutrients are introducing significant lags in the response of surface waters to management actions. Nonpoint nutrient inputs, which are typically dominant in agricultural areas, have not been targeted by U.S. environmental laws in the same way as point discharges.[5] Likewise, targeted efforts in certain areas seem to have been effective but not of sufficient magnitude to decrease nutrient export at larger scales.[34] While legacy nutrients are known to delay the response of surface waters to nutrient management efforts in many systems,[35,36] the effect of legacy nutrients on streamwater quality trends is variable at the national scale[37] In any case, our results indicate that nutrient concentrations remain elevated in agricultural watersheds, which is known to be a pressing water quality problem and stands in contrast to the apparent progress in urban areas (Figure 1).

The near ubiquity of $NH_4^+$ decreases is notable and likely a result of a suite of water quality improvements. More than 80% of sites were found to have likely decreases in $NH_4^+$ (SI Table S2). In developed areas, elevated $NH_4^+$results from the combined effects of N-rich organic matter inputs to streams along with low oxygen concentration. Decreasing inputs of organic matter from ongoing WWTP upgrades or improved erosion control contributed to improvements in water quality[32] and are likely related to the large decreases in $NH_4^+$ concentration. The reasons for decreasing $NH_4^+$ concentrations in agricultural areas are not well-known, but the possibility that they result from a general decrease in nutrients in these areas is dispelled by the results of this analysis (Figures 1 and 2, SI Table S3). Improved handling of point-source discharges from livestock facilities or improved sediment retention could have contributed to this trend. Better sediment retention, which is reflected in the prevalence of decreasing TSS trends in agricultural areas (Figure 3, SI Table S4), decreases the organic matter load while simultaneously allowing greater $NH_4^+$ transformation and uptake through enhanced primary production or greater water column oxidation. For example, $NH_4^+$ uptake in agricultural streams is related to stream primary production, which is highly sensitive to turbidity.[38] In addition, $NH_4^+$ can sorb to sediment particles and thus lower sediment loads may decrease an important route of $NH_4^+$ delivery to surface waters in agricultural areas. In less developed areas, $NH_4^+$ trends have been related to atmospheric deposition, with inconsistent responses across geographic regions,[10] which is consistent with our finding of small and variable changes in $NH_4^+$ among undeveloped sites (Figure 2, SI Table S4).

**Major Ions and Suspended solids.** Concentrations of most major ions were highest at sites draining agricultural watersheds (Figure 3). The exceptions were $Na^+$ and $Cl^-$, which increased rapidly in urban areas during the period 1992−2012; sites in these areas had the highest concentrations by the end of the analysis period. Undeveloped areas also had high concentrations of $Ca^{2+}$, $Na^+$, $Mg^{2+}$, and $SO_4^{2-}$, although SpCond was much lower at undeveloped sites than at agricultural sites (Figure 3). TSS was highest at agricultural and urban sites and lowest at undeveloped sites (Figure 3).

Among all sites included in the analysis, median trend results were positive for all constituents except $SO_4^{2-}$ and TSS, which were negative (Figure 4, SI Table S4). Decreases in $SO_4^{2-}$ were broadly distributed, with likely downward trends at >70%

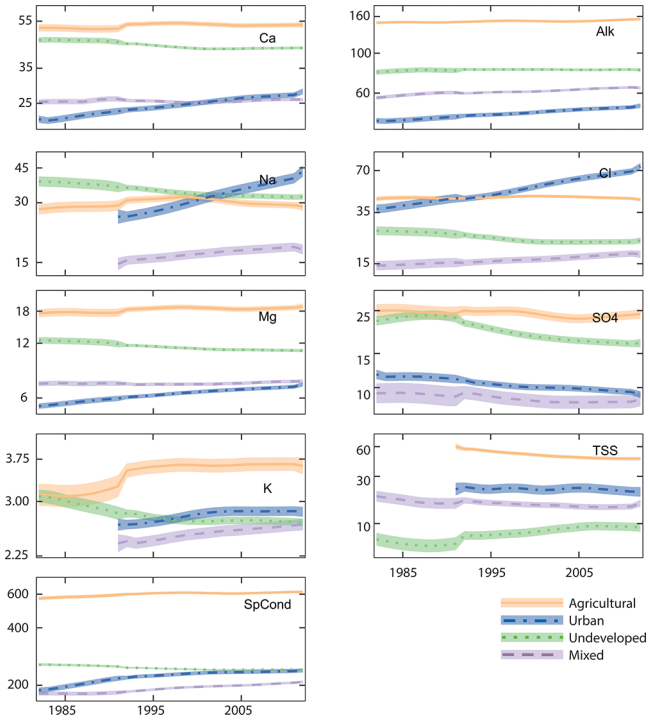


**Figure 3.** Estimated marginal mean of major ions and suspended solids for every year 1982−2012 categorized by land use type. Units are elemental mg $L^{-1}$ of the element for all constituents except specific conductance, which is $\mu$mhos $cm^{-1}$, and alkalinity, which is mg $CaCO_3$ $L^{-1}$. Shaded areas show 95% confidence intervals around the estimated concentration. Note that the *y*-axis is on a log scale. Alk, alkalinity; Ca, calcium; Cl, chloride; K, potassium; Mg, magnesium; Na, sodium; SpCond, specific conductance; $SO_4$, sulfate; TSS, total suspended solids.

of all sites (Figure 4, SI Table S4). For other water quality constituents, trends varied by land use. Positive trends for most major ions were evident at urban sites (Figure 4, SI Table S4). More than two-thirds of urban sites had likely increases in alkalinity, $Ca^{2+}$, $Cl^-$, $Mg^{2+}$, $K^+$, $Na^+$, and SpCond (Figure 4, SI Table S4). In agricultural areas, a large proportion of sites showed likely increases in alkalinity and $Mg^{2+}$ and likely decreases in TSS, while more mixed results were found for other constituents (Figure 4). Sites in mixed land use also showed likely increases in many constituents, similar to urban sites, although the magnitude of change was much smaller (Figure 4, SI Table S4). In contrast to the other land use types, undeveloped areas showed a greater tendency for decreases in major ions. More than half of sites in undeveloped areas showed evidence of decreasing trends in all constituents except TSS and SpCond (Figure 4, SI Table S4). In addition, $SO_4^{2-}$ concentrations decreased at >90 of sites in undeveloped areas and showed the largest median decrease over the period 1992−2012, - 4.6 mg $L^{-1}$ (Figure 4, SI Table S4).

The widespread decreases in $SO_4^{2-}$ (Figure 3) reflect the decades-long decreases in atmospheric deposition of sulfur in the U.S.[39] Lags in the storage and release of $SO_4^{2-}$ in watersheds complicates this interpretation.[40] But declining acidic deposition has been linked to $SO_4^{2-}$ trends in rivers in the U.S. and elsewhere.[8,41] While $SO_4^{2-}$ itself is not considered a pollutant and is only regulated as a secondary pollutant by the U.S. Environmental Protection Agency, it can be indicative of changes in acid deposition, which has far-reaching implications for water quality and ecosystem health. Therefore,


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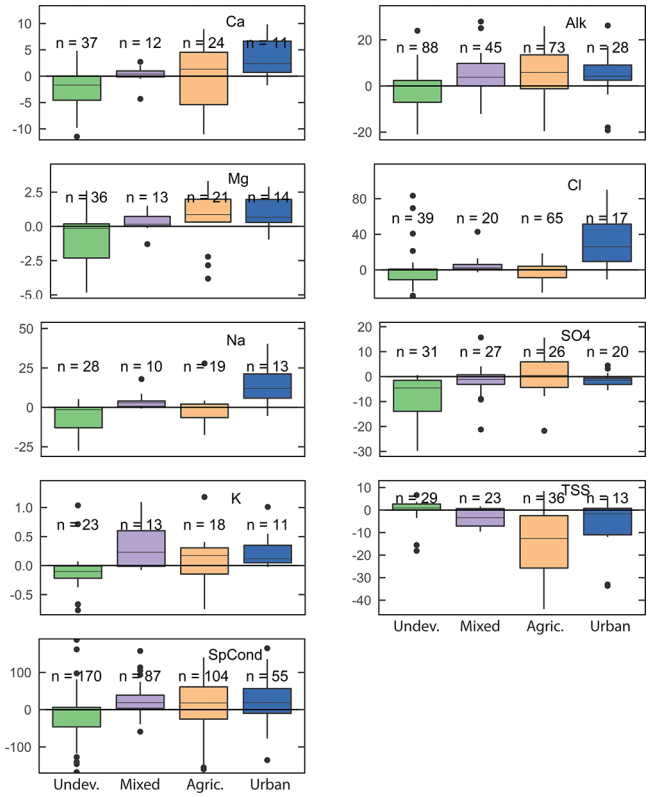


**Figure 4.** Boxplots of the change in concentration (1992−2012) of major ions and suspended solids. Units are mg $L^{-1}$ of the element for all constituents except SpCond, which is $\mu$mhos $cm^{-1}$, and alkalinity, which is mg $CaCO_3$ $L^{-1}$. Values below 0 represent decreases and values above 0 represent increases.

we interpret declining $SO_4^{2-}$ concentrations as improvements to water quality. This result suggests a system-wide improvement in water quality due to targeted efforts associated with the 1990 Clean Air Act Amendments, which established the Acid Rain Program and sought to decrease acid deposition in the U.S..

One of the most striking trends was the dramatic increase in SpCond in all human-dominated landscapes (Figure 3, SI Table S4). This pattern has been noted in other studies and the process driving the trend differs situationally and in relation to the predominant land use. Increasing ions in urban areas have been attributed to road salt application, concrete weathering, point source contributions, and increased chemical weathering rates due to soil disturbance.[13,42,43] Liming of agricultural lands adds weatherable substrates and the overall chemical weathering rate can be enhanced due to soil disturbances and additions of N-containing fertilizers.[44,45] In drier environments, irrigation can also result in surface water salinization through the addition of salts in the irrigation water which are then concentrated by evaporation.[46,47] Both of these processes can lead to an increase in ion concentration in agricultural streams.

The need to understand and potentially manage the salinity of inland waters is becoming increasingly clear. The salinity of water used for irrigation in arid and semiarid environments has been the focus of extensive management efforts. However, there is a growing recognition that increasing ionic strength of waters in other environments can have significant ecological and human health consequences as well.[48] Altered salinity can be a major stress on stream biota, increased chloride concentrations can affect the corrosivity of source waters, salt additions can lead to loss of exchangeable cations in soil, and the mobility and toxicity of some pollutants, especially metals, can be enhanced at high salt concentrations.[13,49] Furthermore, salt pollution can enter groundwaters, which can become dominant water sources at baseflow and thereby affect biota during low-flow times of the year when they may be most sensitive to fluctuations in water quality.[44] Increasing SpCond, particularly when it is dominated by $Cl^-$, is an insidious problem that is linked to human health concerns. Elevated chloride concentrations encourage corrosion of lead and copper pipes and have been linked to problems of lead contamination in drinking water facilities.[17] $Cl^-$ is difficult to remove using typical drinking water treatment processes, such as coagulation, filtration, or pH adjustments, and so can have system-wide effects from source waters to the tap.[16]

The evolving nature of water quality in the U.S. is especially evident when the EMM of nutrients and $Cl^-$ are viewed together (Figure 5). Increasing $Cl^-$ is common at urban, agricultural, and mixed land use sites whereas only urban areas have experienced broad decreases in TN and TP (Figure 5). Nutrient concentrations remain elevated in urban areas but have decreased greatly when compared to the early part of the record. Measures to reduce phosphorus loading from WWTPs,

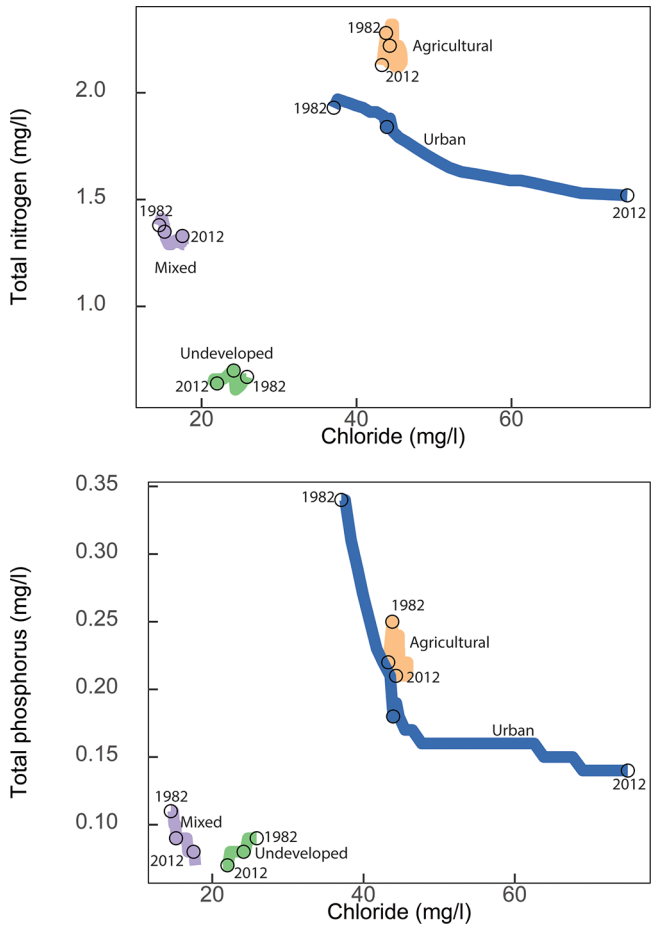


**Figure 5.** Estimated marginal mean of total nitrogen or total phosphorus plotted against chloride by land use type (agricultural, urban, undeveloped, or mixed). Circles denote EMM for each land use type in 1982, 1992, and 2012 with the earliest and latest years labeled on the figure.


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such as controls on phosphorus content of soap, secondary treatment, and phosphorus removal in WWTPs, have been implemented in many parts of the U.S.[50] and have apparently resulted in decreases in TP concentration in the most developed areas. Likewise, the population served by advanced WWTPs, which can reduce TN loading to streams, has grown tremendously in the past decades and now surpasses 100 million.[51] In contrast, major ion inputs have increased in human-dominated landscapes and resulted in noticeable increases in these solutes (Figure 3, Figure 5).

This study underscores the rapid and multifaceted changes that are facing U.S. rivers. Despite the apparent successes of targeting point sources of pollution and decreasing acid deposition, the threats to our water supplies are evolving. Water quality regulations and best management practices designed to address the problems of excess nutrients and sediments in surface waters are not adequate to curtail the growing problem of salinization, which is driven by different sources. More research is needed to understand how increases in salinity, and in specific major ion concentrations, might be affecting aquatic ecology and ecosystem services. Regular, broad, large-scale studies are crucial to provide appropriate context of the largest changes in water quality and can serve as a basis for up-to-date research and decision-making to respond appropriately to the most important threats facing water supplies for human and ecological well-being.

## ■ ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.est.9b05344.

> Map of sites included in the analysis. Example of *estimated marginal means* for one water quality constituent. Table of definitions used for land use categorization. Tables of trend results for all sites and for sites broken out by land use type (PDF)

## ■ AUTHOR INFORMATION


### Corresponding Author

**Edward G. Stets** − *U.S. Geological Survey, Earth System Process Division, Boulder, Colorado 80303, United States;* orcid.org/0000-0001-5375-0196; Email: estets@usgs.gov

### Authors

**Lori A. Sprague** − *U.S. Geological Survey, Earth System Process Division, Lakewood, Colorado 80225, United States;* orcid.org/0000-0003-2832-6662

**Gretchen P. Oelsner** − *U.S. Geological Survey, New Mexico Water Science Center, Albuquerque, New Mexico 87113, United States*

**Hank M. Johnson** − *U.S. Geological Survey, Oregon Water Science Center, Portland, Oregon 97201, United States;* orcid.org/0000-0002-7571-4994

**Jennifer C. Murphy** − *U.S. Geological Survey, Lower Mississippi-Gulf Water Science Center, Nashville, Tennessee 37211, United States*

**Karen Ryberg** − *U.S. Geological Survey, Dakota Water Science Center, Bismarck, North Dakota 58503, United States*

**Aldo V. Vecchia** − *U.S. Geological Survey, Dakota Water Science Center, Bismarck, North Dakota 58503, United States*

**Robert E. Zuellig** − *U.S. Geological Survey, Colorado Water Science Center, Denver Federal Center, Lakewood, Colorado 80225, United States*

**James A. Falcone** − *U.S. Geological Survey, Earth System Process Division, Reston, Virginia 20192, United States*

**Melissa L. Riskin** − *U.S. Geological Survey, New Jersey Water Science Center, Lawrenceville, New Jersey 08648, United States*

Complete contact information is available at: https://pubs.acs.org/10.1021/acs.est.9b05344


### Notes

The authors declare no competing financial interest.

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