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Trends in stream nitrogen concentrations for forested reference catchments across the USA

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Abstract
To examine whether stream nitrogen concentrations in forested reference catchments have changed over time and if patterns were consistent across the USA, we synthesized up to 44 yr of data collected from 22 catchments at seven USDA Forest Service Experimental Forests. Trends in stream nitrogen presented high spatial variability both among catchments at a site and among sites across the USA. We found both increasing and decreasing trends in monthly flow-weighted stream nitrate and ammonium concentrations. At a subset of the catchments, we found that the length and period of analysis influenced whether trends were positive, negative or non-significant. Trends also differed among neighboring catchments within several Experimental Forests, suggesting the importance of catchment-specific factors in determining nutrient exports. Over the longest time periods, trends were more consistent among catchments within sites, although there are fewer long-term records for analysis. These findings highlight the critical value of long-term, uninterrupted stream chemistry monitoring at a network of sites across the USA to elucidate patterns of change in nutrient concentrations at minimally disturbed forested sites.

Keywords: nitrate, ammonium, trends, stream, forested catchment, reference catchments
S Online supplementary data available from stacks.iop.org/ERL/8/014039/mmedia

1. Introduction

Human alteration of the nitrogen (N) cycle is a major environmental issue that crosses spatial scales from the

catchment to the globe. Energy and food production have led to a ten-fold increase in reactive forms of N in terrestrial ecosystems from 1860 to 2005 (Galloway *et al* 2008). Reactive N is routed to freshwaters through surface runoff and groundwater discharge or atmospheric deposition, resulting in alteration of the forms and concentrations of N species, which may result in aquatic eutrophication and altered stream functions (Stoddard 1994). Despite the implementation of the Clean Water Act (1972) and the Clean Air Act (1970), stream and groundwater N concentrations have continued to increase in large areas of the USA during recent decades (Smith *et al* 1987, Lettenmaier *et al* 1991, Rupert 2008, Sprague *et al* 2011) and have been predicted to further increase in the future (Howarth *et al* 2002). However, much of what is known about temporal changes in stream water quality originates from studies where catchments have been altered by land use and land cover change.

In contrast, we know little about temporal trends in N dynamics at forested, headwater streams with minimal human impacts, even though they serve as a benchmark against which we can evaluate more heavily human-modified catchments. Trends in stream-water nutrients in the relative absence of changes in land use or land cover can be evaluated using long-term data from unmanaged forested headwater (i.e. reference) catchments, such as those in the USDA Forest Service Experimental Forests and Ranges (EFR) network. These datasets represent the most complete information available on stream N concentration for reference sites because of their length (e.g., Hubbard Brook Experimental Forest, HJ Andrews and Coweeta Hydrologic Laboratory have been analyzing stream chemistry since 1963, 1969, and 1972 respectively), because of their sampling frequency (i.e., at least biweekly for all sites except HJ Andrews where they collect three-weekly composite samples), and finally because of their spatial coverage (EFRs encompass a suite of climates and forest types across the USA). Data from these reference catchments are frequently used in paired watershed comparisons to evaluate effects of land use treatments, assuming that in the absence of the perturbation under study, both the reference and treatment catchments would behave similarly.

Although stream chemistry trends in reference catchments have been investigated at individual EFRs, a comparison of trends in reference sites across the country has not occurred. Researchers at both Coweeta Hydrologic Laboratory in North Carolina (Swank and Vose 1997) and Fernow Experimental Forest in West Virginia (Peterjohn *et al* 1996) observed increased stream N over the last decades in reference catchments and attributed the trend to higher N deposition, and changes in nutrient demand and forest succession within catchments. At the Hubbard Brook Experimental Forest in New Hampshire, stream nitrate concentrations have been declining in recent decades after increasing from 1963 into the 1970s (Likens and Bormann 1995, Campbell *et al* 2007). These trends in stream nitrate at Hubbard Brook have not been explained by changes in atmospheric deposition and are thought to be due in part to the long-lasting effect of forest cutting in the early 1900s combined with effects of changing climate (Bernal *et al* 2012).

Further, little is known about the synchrony of trends among adjacent catchments within EFRs. Our study fills this gap by analyzing trends in stream nitrate (NO_3–N) and ammonium (NH_4–N) concentrations from forested reference catchments in multiple EFRs across the USA. To evaluate if stream N trends were synchronous with trends in likely drivers, we examined correlations between trends in stream N, streamflow, and ammonium and nitrate concentration in atmospheric wet deposition.

2. Methods

We analyzed stream inorganic N from 22 independent forested reference catchments in seven EFRs across the continental USA and Puerto Rico (figure 1(a)); these span a wide range of climatic, hydrologic and vegetation conditions (table S1 available at stacks.iop.org/ERL/8/014039/mmedia). Each catchment had a minimum of 12 yr of consistent, high frequency stream chemistry data, daily streamflow data, and weekly wet deposition chemistry collected nearby. These catchments are considered reference because they have not experienced direct anthropogenic disturbances other than atmospheric deposition during the last 60 yr. A total of 559 yr of stream nitrate and 523 yr of stream ammonium data collected at least biweekly were analyzed.

Trends were analyzed using the Seasonal Kendall test (Hirsch *et al* 1982). This non-parametric, rank test has been proven robust in evaluating trends in time series that have strong seasonality. We selected this test because, in comparison to other trend analysis methods (e.g., linear regression, time series analysis, etc), the Seasonal Kendall test does not make assumptions about the distribution of the data and allows missing values and censored data without biasing the analysis (Helsel 2005). The Seasonal Kendall test is an extension of the Mann–Kendall test for monotonic trends (Mann 1945). If $(x_1, y_1), (x_2, y_2), \ldots, (x_n, y_n)$ are observations where X is time and Y is the object variable, the Kendall S statistic can be computed from each data pair as:

$$S = P - N$$

where P is the number of $Y_i < Y_j$ for all $i < j$ and N is the number of $Y_i > Y_j$ for $i < j$.

S has a mean of zero and variance:

$$\sigma^2 = [n(n-1)(2n+5) - \Sigma t(t-1)(2t-5)]/18$$

where t is the number of data pairs involved at any given time. All observations below the detection limit are considered tied, and the differences of all tied pairs are zero. The Seasonal Kendall accounts for the effects of seasonality on trends by combining the Mann–Kendall test computed on each of the seasons separately (Hirsch *et al* 1982). Seasonal Kendall tau ranges between -1 and $+1$ and is the ratio of the number of positive differences minus the number of negative differences to the number of pairs (discounted for ties). If there is enough disparity between the number of positive and negative differences, then tau is statistically significant.

We analyzed trends in monthly flow-weighted concentrations of nitrate and ammonium in streams, monthly

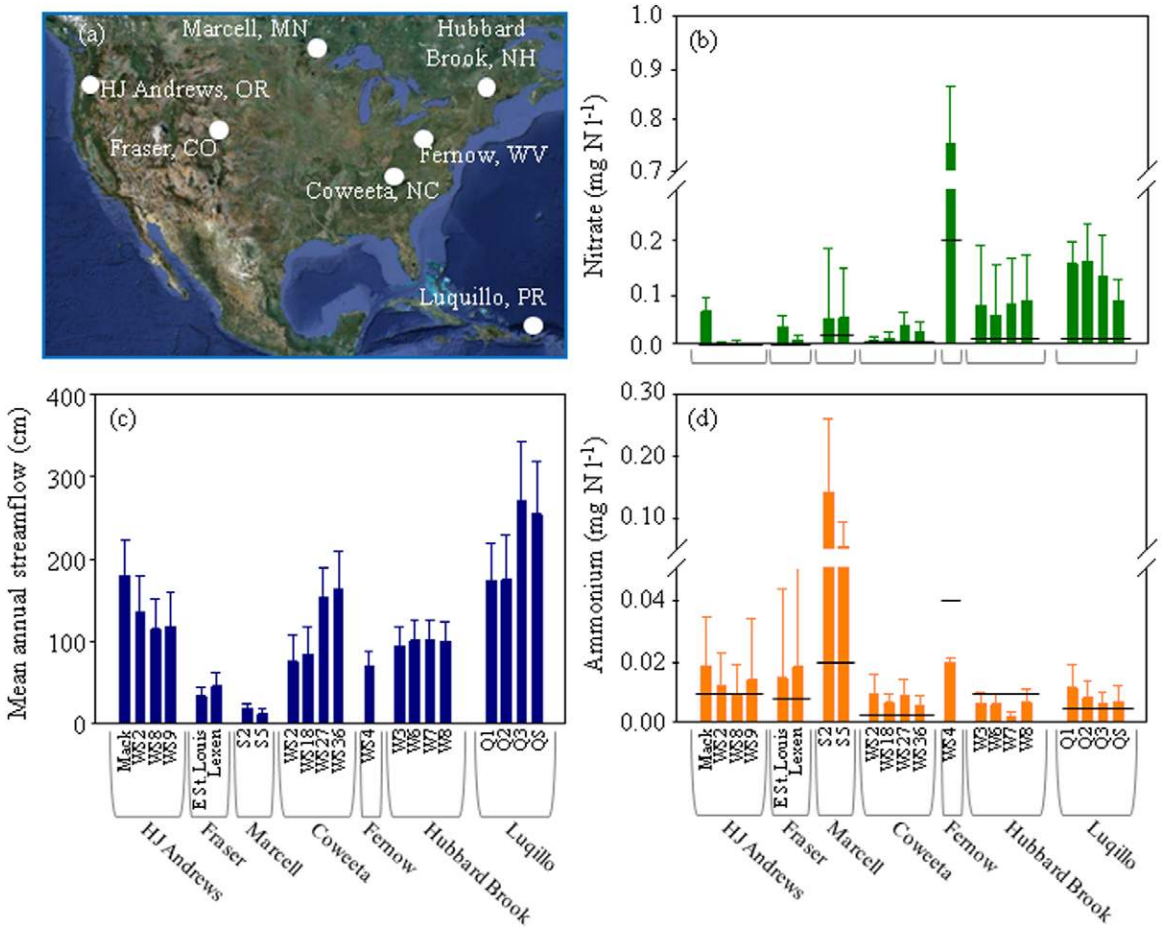

Figure 1. (a) Locations of the Experimental Forests included in this study; averages from 1996 to 2007 are shown for (b) mean monthly flow-weighted stream nitrate concentration, (c) mean annual streamflow, and (d) mean monthly flow-weighted stream ammonium concentration in study catchments. Error bars are standard deviations of the mean. Horizontal black lines in (b) and (d) indicate minimum detection limits. The mean and standard deviation were calculated from censored values after replacing all values below detection limit by half of the maximum detection limit observed per site between 1996 and 2007.

nitrate and ammonium concentration in wet deposition, and monthly streamflow (see table S2 available at stacks.iop.org/ERL/8/014039/mmedia for more details about sampling frequency, flow-weighted concentration calculations, and detection limits). Prior to the analysis, stream concentrations for each site were censored so that the highest detection limit during the analysis period was used consistently. The magnitude of the trend was assessed using the Sen slope (Sen 1968) which report the median change in value versus time (slope) of all the possible pairs in the dataset including zero differences. The existence of a significant trend with a Sen slope of zero is possible when a large number of observations are below the detection limit and therefore considered tied. The analyses were performed in R v2.13 using the 'Wq' and 'Kendall' packages with a threshold for significance set to $p < 0.05$. To standardize analyses among catchments and sites, trends were calculated for three different periods (calendar years from 1996 to 2007, 1987 to 2007, and 1972 to 2007), except for wet deposition. The longest period analyzed for trends in wet deposition began in 1980 for the Andrews, 1985 for Luquillo, and 1978 for the rest of the sites.

To evaluate more fully the influence of the length and period of the data record on trend detection, we conducted additional analyses on stream N concentrations from HJ Andrews and Hubbard Brook catchments. After analyzing trends for a minimum period (1996–2007), we iteratively reanalyzed trends after increasing the length of record in 1 yr increments for the full data record (1969–2007 for HJ Andrews, 1964–2007 for Hubbard Brook).

To understand how trends in stream N relate to trends in streamflow or to trends in N in wet deposition at a national level, we performed correlation analyses (Kendall's tau) between the Sen slopes for stream nitrate concentrations versus the Sen slopes for the potential drivers (i.e., streamflow, ammonium and nitrate concentration in atmospheric wet deposition) as well as stream ammonium versus potential drivers.

3. Results

From 1996 to 2007, mean stream nitrate concentrations at all EFR study catchments except Fernow were $\leq$0.16 mg NO_3–N l^{-1}; average nitrate at Fernow was 0.75 mg

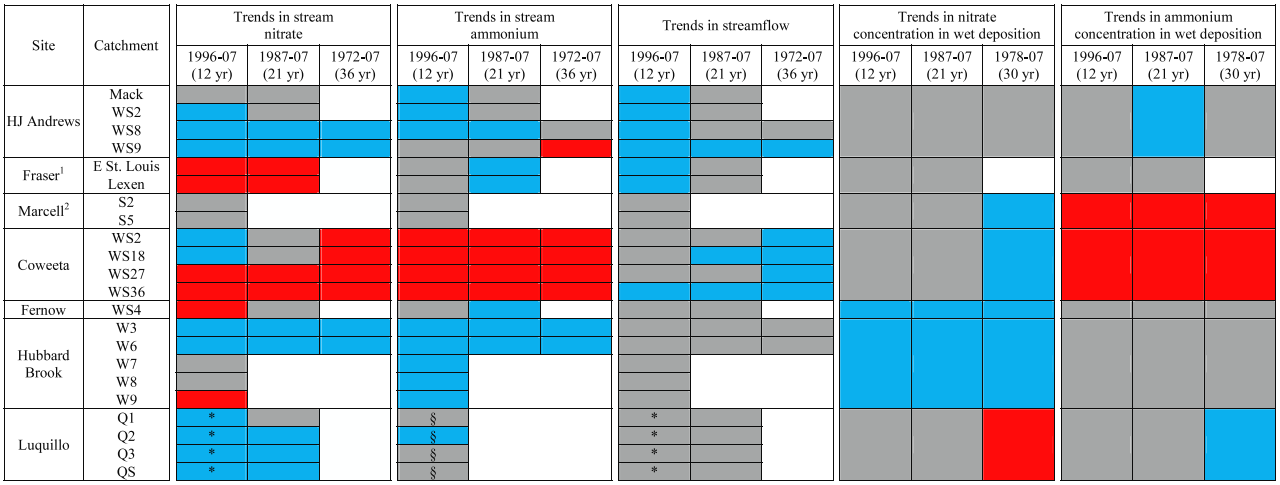

Figure 2. Observed trends in monthly flow-weighted nitrate and ammonium concentration, streamflow, and nitrate and ammonium concentration in wet deposition for three time periods, calculated using Seasonal Mann–Kendall. Red denotes increasing trends, gray denotes no significant trends, and blue denotes decreasing trends for that period of time and catchment.

NO_3–N l^{-1} (figure 1(b)). Ammonium concentrations in streams were equal to or below 0.01 mg NH_4–N l^{-1} at 19 of the 21 study catchments; concentrations higher than 0.01 mg NH_4–N l^{-1} were observed at Marcell (0.14 mg NH_4–N l^{-1} at S2 and 0.05 mg NH_4–N l^{-1} at S5). Most of the ammonium values were below detection at Fernow and Hubbard Brook (figure 1(d)). Catchments showed a wide range of mean annual streamflow, ranging from a low of 10.7 cm at Marcell-S5 to a high of 269.2 cm at Luquillo-Q3 (figure 1(c)). Mean annual wet deposition of dissolved inorganic N was highest at Fernow (5.6 kg ha^{-1}) and lowest at HJ Andrews (0.9 kg ha^{-1}; table S1 available at stacks.iop.org/ERL/8/014039/mmedia).

3.1. Trends over time in stream N concentrations

Stream nitrate concentrations, during the 1996–2007 period, significantly decreased in 11 of 22 reference catchments, increased in six, and showed no trend in five (figure 2). From 1987 to 2007, nitrate concentrations significantly decreased in seven of 17 catchments and significantly increased in four catchments. Over the 36 yr period between 1972 and 2007, the four Coweeta catchments showed significant increasing trends and the two catchments at Hubbard Brook and the two at HJ Andrews showed significant decreasing trends (figure 2). The slopes of the observed significant trends ranged between −10 and 8.2 μg NO_3–N l^{-1} yr^{-1} (figure S1 available at stacks.iop.org/ERL/8/014039/mmedia).

Stream ammonium concentrations, during the 1996–2007 period, significantly decreased in nine of 22 catchments and increased in four. From 1987 to 2007, six of 13 catchments showed significant decreasing trends and four showed significant increasing trends. During the 36 yr period between 1972 and 2007, five of eight catchments (the four Coweeta catchments and HJ Andrews-WS9) showed significant increasing trends, and the two catchments at Hubbard Brook showed decreasing trends (figure 2). The slopes of the observed significant trends ranged between −0.7 and 0.8 μg NH_4–N l^{-1} yr^{-1} (figure S1 available at stacks.iop.org/ERL/8/014039/mmedia).

Within an EFR site, some reference catchments that were close to each other displayed opposite trends in stream N during the same time periods. For example, during the shortest time period evaluated (1996–2007), stream nitrate decreased at Coweeta-WS2 and Coweeta-WS18 but increased at Coweeta-WS27 and Coweeta-WS36 (figure 2). Similarly, during the 1983 and 1984–2007 period, stream ammonium decreased at HJ Andrews-WS8 and increased for HJ Andrews-Mack and HJ Andrews-WS2 (figures 3(g)–(j)).

Trends at some individual catchments were consistent over the entire period of collection (e.g., negative nitrate trends at HJ Andrews-WS9; figure 3(f)), whereas trends at other catchments changed direction depending upon the length of record analyzed. For example, HJ Andrews-Mack showed increasing stream ammonium concentrations when analyzing 25, 24, 23, 22 or 21 yr of record prior to 2007; no significant changes in stream ammonium when considering 20–13 yr of record; and decreasing stream ammonium concentration when analyzing 12 yr of record (figure 3(g)). In addition, the shift between positive and negative trends did not occur simultaneously among catchments or in nitrate and ammonium concentrations.

3.2. Associated trends and relationships between them

Streamflow showed significant decreasing trends at HJ Andrews, Fraser, and Coweeta-WS36 during the 1996–2007

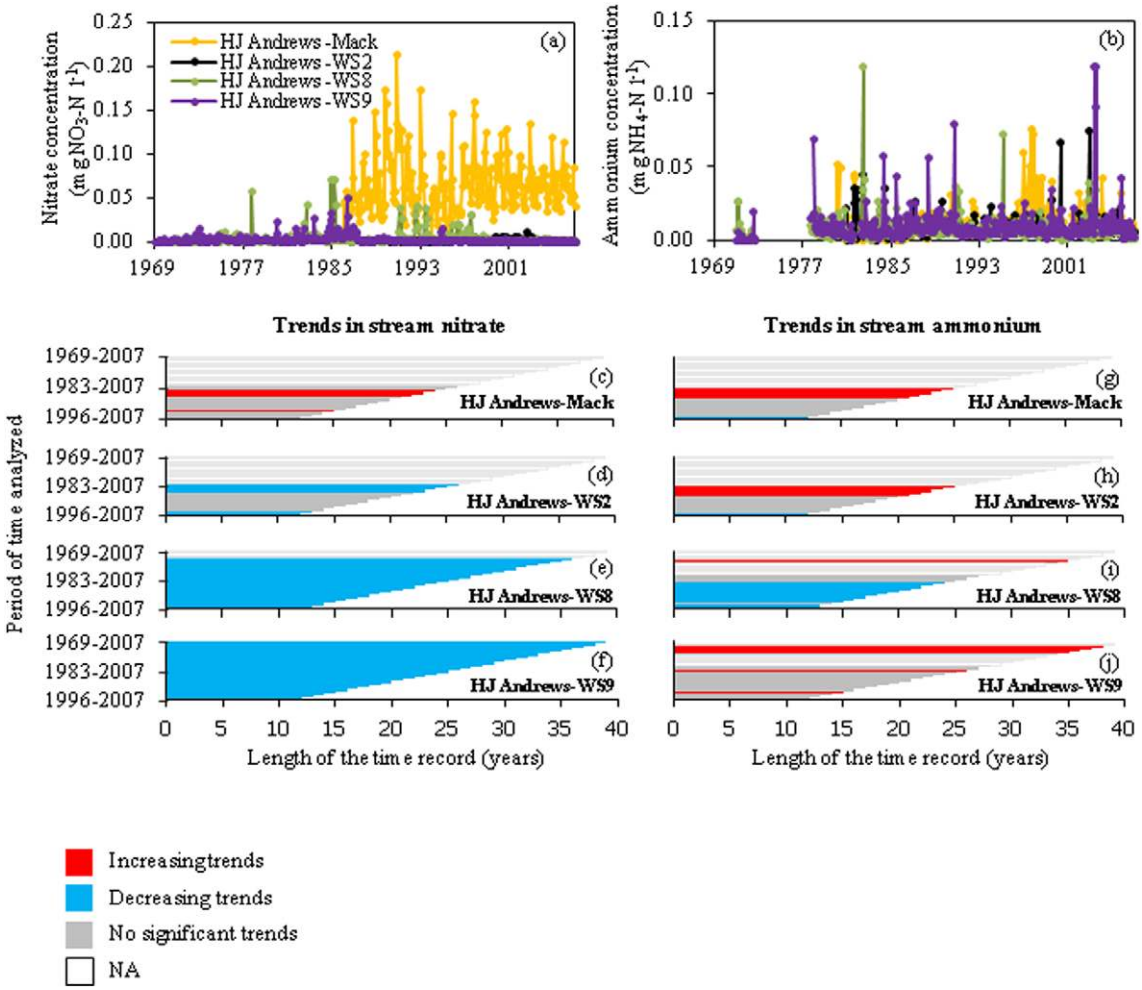

Figure 3. Mean monthly flow-weighted (a) stream nitrate and (b) stream ammonium concentrations at HJ Andrews and trends in (c)–(f) nitrate and (g)–(j) ammonium concentrations at four HJ Andrews catchments. Trends are calculated for the recent 12 yr and then for longer periods by adding successive 1 yr increments. Red denotes increasing trends, gray denotes no significant trends, and blue denotes decreasing trends.

period, at HJ Andrews-WS9, Coweeta-WS18 and WS36 during the 1987–2007 period, and at HJ Andrews-WS9 and Coweeta catchments during the 1972–2007 period (figure 2).

Average monthly nitrate concentration in wet deposition decreased at Hubbard Brook and Fernow during all three time periods, decreased at Coweeta and Marcell during the 1978–2007 period, and increased at Luquillo during the 1985–2007 period. Average monthly ammonium concentrations in wet deposition increased at Coweeta and Marcell during the three time periods and decreased at HJ Andrews during the 1980–2007 period, and decreased at Luquillo during the 1985–2007 period (figure 2).

Trends in stream nitrate concentration were negatively correlated with trends in streamflow across the eight catchments with data during the 1972–2007 period (Kendall's tau $= -0.714, p = 0.013, n = 8$), but not across all catchments over the shorter time periods evaluated. No relation was detected between trends in stream nitrate concentration and nitrate concentration in wet deposition at a national level. Trends in stream ammonium concentration were negatively correlated with trends in streamflow (Kendall's tau $= -0.622, p = 0.005, n = 13$) and positively correlated to trends in ammonium concentration in wet deposition (Kendall's tau $= 0.620, p = 0.010, n = 13$) at a national level during the 1987–2007 period. The figures representing nitrate concentration versus time at each of the sites and the complete analysis of trends for Hubbard Brook can be found in section S3 at stacks.iop.org/ERL/8/014039/mmedia.

4. Discussion

Long-term data from reference forested catchments provide a unique opportunity to evaluate complex patterns of stream N concentrations over more than four decades across the USA. Through synthesis of data from 22 reference catchments at seven EFRs, we find that there are trends in stream N concentrations even at these minimally disturbed reference sites and that they present considerable spatial and temporal variability both among catchments within sites and among sites.

4.1. Spatial and temporal variability in trends

Nitrogen in human-altered streams and rivers of USA has been shown to increase during recent decades (Smith

et al 1987, Richards and Baker 1993, Johnson *et al* 2009, Dubrovsky *et al* 2010). However, in the reference forested streams of the Northeast (Hubbard Brook), we found decreasing trends in stream nitrate, which supports the previous findings of Likens and Bormann (1995) and Campbell *et al* (2007) for Hubbard Brook and Goodale *et al* (2003) for the White Mountain region of New Hampshire. Stream nitrate also declined in the Pacific Northwest (HJ Andrews) and in Puerto Rico (Luquillo). Still, these trends are not consistent at national or at local scales, since Fraser in the Mountain West, and Fernow and half of the Coweeta catchments in the South, showed increasing trends in nitrate, suggesting that the controls on stream N concentrations vary spatially among sites.

Adding to these complex spatial patterns of trends, catchments within an EFR sometimes had opposing trends for the same N species for the same period of time. For example, we found opposing trends in stream nitrate concentrations among catchments within Coweeta from 1996 to 2007 and in stream ammonium at HJ Andrews from 1983/1984 to 2007. Over longer time scales, trends among catchments within sites tended to be more consistent, although fewer long-term records were available for these analyses. Additionally, stream nitrate and ammonium did not show consistent trends or coincident timing in trend shifts. Because catchments from the same site do not necessarily present the same direction in trends during the same time period, extrapolation of trends in space or across species of N should be made with extreme prudence.

The length of record is a major factor influencing detection of trends; trends for several catchments were not consistent over time. The inclusion of additional years in the time series analyzed shifted the direction or significance of trends in a number of catchments. This highlights that even when trends for short periods are statistically significant, they are not necessarily indicative of longer-term patterns. Therefore, there is need for caution in extrapolating trends over time. It is also important to recognize that statistically significant trends, even using the Seasonal Kendall test which is more robust than regressions for analysis of trends, might be ecologically insignificant. If the magnitude of change is extremely small, such as observed for stream nitrate at the HJ Andrews or stream ammonium at Hubbard Brook (figure S1 available at stacks.iop.org/ERL/8/014039/mmedia), the impacts of a significant trend on processes or functions may be minimal.

Our data are unique because they represent high frequency data of at least biweekly long-term sampling from reference sites. The detectability of trends depends on each site's ability to precisely analyze solutes, but because of the improvement of analytical methods over the duration of these studies, detection limits may change over time. By recensoring monthly flow-weighted concentrations prior to the analysis and using the highest detection limit for the full period included in the analysis: we avoided trend artifacts. This meant that we were able to evaluate long-term trends that were not influenced by differing detection limits over time.

4.2. N concentrations and magnitude of trends

In general, stream N concentrations at the forested reference catchments included in this study were low in comparison to concentrations found in urban or agricultural streams and in the lower range of undisturbed catchments reported by other studies (Clark *et al* 2000, Binkley *et al* 2004). In contrast to what has been recently observed nationwide (Sprague *et al* 2009), stream nitrate concentrations in our forested reference sites showed a higher proportion of significant trends (77% this study, 33% Sprague *et al* 2009) and a higher tendency for decreasing trends in stream nitrate (50% this study, 27% Sprague *et al* 2009). The slopes of the trend observed in our reference streams (between −10 and 8.2 μg NO_3–N l^{-1} yr^{-1}) were in the middle range of those observed by Sprague *et al* (2009) between 1993 and 2003 in streams with similar mean nitrate concentrations (between −31.7 and 40.0 μg NO_3–N l^{-1} yr^{-1}). However, the relative magnitude of change in stream N concentrations should be considered when interpreting trends over time. For instance, during the 1996–2007 period, stream nitrate at Coweeta-WS2 and Coweeta-WS18 decreased by 0.3 μg NO_3–N l^{-1} yr^{-1} while increases of 1.6 and 0.8 μg NO_3–N l^{-1} yr^{-1} were observed at Coweeta-WS27 and WS36, respectively. This variability in the absolute magnitude of change is reduced when comparing the percentage of change of the mean (−4% yr^{-1}, −2% yr^{-1}, 4% yr^{-1} and 3% yr^{-1} at Coweeta-WS2, WS18, WS27 and WS36, respectively).

Ammonium concentrations in our study were less than nitrate concentrations, except at the peatland catchments of Marcell. Likewise, ammonium concentrations showed a smaller range of variation among catchments, results also observed by Clark *et al* (2000) and Binkley *et al* (2004). At some sites, ammonium values were close to the detection limit. This would help to explain the high variability in trends from year to year in the detailed analysis of HJ Andrews ammonium data, where small changes in N transformation pathways within a catchment might result in changes in trends. Additionally, data that are below the detection limit (which end up as ties in the ranking for the analysis of trends) coupled with occasional detectable concentrations might explain significant ammonium trends with a slope of 0 μg N l^{-1} yr^{-1} at Hubbard Brook or Fernow.

4.3. Possible drivers of changes in stream N

Trends in stream N concentrations were not synchronous with trends in potential drivers such streamflow or N concentrations in wet atmospheric deposition. Some of the correlations between trends were significant for one time period and not significant for others, indicating a possible temporal change in the variables driving those trends. Moreover, the lack of consistent correlations between trends in stream N concentrations and N in wet deposition reflects transformations that N species entering the catchment undergo both in the terrestrial and aquatic ecosystems.

Unlike trends observed in other broad-scale studies (e.g., Smith *et al* 1987 or Sprague *et al* 2009), trends in

stream N concentrations in our reference catchments should reflect changes in stream N concentrations that are not related to anthropogenic perturbations other than atmospheric deposition. The observed changes in stream N concentrations most likely reflected effects of change in climatic drivers, such as hydrology and temperature. Changes in streamflow (Lins and Slack 1999) and in the timing and magnitude of precipitation (Pielke and Downton 2000), could lead to changes in the relationship between N transport per unit of water volume (e.g., a relatively constant amount of N being transported by changing quantity of streamflow would lead to a changing trend in stream N concentration). Additionally, changing hydrology may affect N availability and transformation processes (Dahm *et al* 2003). Changes in air temperature, although not always paralleled to changes in stream-water temperature (Arismendi *et al* 2012), would affect microbial activity and N cycling rates within the catchment (Brookshire *et al* 2011). Moreover, stream N concentration is expected to change during forest succession, as a result of changing net ecosystem productivity as a forest ages (Vitousek and Reiners 1975, Vitousek 1977, Goodale *et al* 2003). Therefore, some of the observed trends could be caused by forest successional dynamics, including long-lasting legacy effects of past anthropogenic events (Bain *et al* 2012) or natural disturbances (Rhoades *et al* 2013, supplementary material S1 available at stacks.iop.org/ERL/8/014039/mmedia). Local catchment factors, including aspect, micrometeorology, vegetation, geology, soils, and natural disturbances can affect how N is transported and processed in catchments and ultimately, influences trends in N concentrations. These findings suggest that even in reference catchments, N concentrations in these streams are not necessarily stationary over time (Milly *et al* 2008).

5. Conclusions

Understanding whether nutrient concentrations are changing over time in reference streams is vital for good management and protection of water resources. The data presented here provide a unique opportunity to document changes in N concentrations in streams in the absence of changes in land use or other anthropogenic impacts except atmospheric deposition. Trends in stream N concentrations show high spatial variability both within and among sites, and our results demonstrate the transient nature of trends. The direction and significance of trends varied with record length at some catchments, a finding that reinforces the value of long data records, the need of properly pairing record lengths for catchment comparisons and the importance of caution when extrapolating trends from short time periods to longer periods.

Synthesis of long-term stream chemistry data from multiple catchments is valuable for understanding trends and for determining spatial variation across the USA, while showing some perils of broadly extrapolating information from individual catchment studies or short data records. Local factors including catchment characteristics and natural disturbance events influence trends within a site. Differences of trends within and among EFRs highlight a need for considering multiple reference catchments at both site and national levels to serve as benchmarks against which we can evaluate more heavily human-modified ecosystems. Reference catchments are also essential to improve our basic understanding of patterns and processes governing element cycles within intact ecosystems. Both of these functions can inform the management of N-pollution effects (e.g. through establishment of water quality standards or total maximum daily loads). These results also emphasize the importance of site-specific strategies that are relevant to choice of catchments and sampling schemes; such information is vital when considering trends, the refinement of existing programs, and establishment of new monitoring sites.

Acknowledgments

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References

Arismendi I, Johnson S L, Dunham J B, Haggerty R and Hockman-Wert D 2012 The paradox of cooling streams in a warming world: regional climate trends do not parallel variable local trends in stream temperature in the Pacific continental United States *Geophys. Res. Lett.* **39** L10401

Bain D J, Green M B, Campbell J L, Chamblee J F, Chaoka S, Fraterrigo J M, Kaushal S S, Martin S L, Jordan T E and Parolari A J 2012 Legacy effects in material flux: structural catchment changes predate long-term studies *BioScience* **62** 575–84

Bernal S, Hedin L O, Likens G E, Gerber S and Buso D C 2012 Complex response of the forest nitrogen cycle to climate change *Proc. Natl Acad. Sci. USA* **109** 3406–11

Binkley D, Ice G G, Kaye J and Williams C A 2004 Nitrogen and phosphorus concentrations in forest streams of the United States *J. Am. Water Resources Assoc.* **40** 1277–91

Brookshire E N J, Gerber S, Webster J R, Vose J M and Swank W T 2011 Direct effects of temperature on forest nitrogen cycling revealed through analysis of long-term watershed records *Glob. Change Biol.* **17** 297–308

Campbell J L, Driscoll C T, Eagar C, Likens G E, Siccama T G, Johnson C E, Fahey T J, Hamburg S P, Holmes R T and Bailey A S 2007 Long-term trends from ecosystem research at the Hubbard Brook experimental forest *Gen. Tech. Rep NRS-17* (Newtown Square, PA: USDA, Forest Service Northern Research Station)

Clark G M, Mueller D K and Mast M A 2000 Nutrient concentrations and yields in undeveloped basins of the United States *J. Am. Water Resources Assoc.* **36** 849–60

Dahm C N, Baker M A, Moore D I and Thibault J R 2003 Coupled biogeochemical and hydrological responses of streams and rivers to drought *Freshwater Biol.* **48** 1219–31

Dubrovsky N M *et al* 2010 *The Quality of Our Nation's Water: Nutrients in the Nation's Streams and Groundwater, 1992–2004* (*US Geological Survey Circular* vol 1350) (Washington, DC: US Department of the Interior)

Galloway J N, Townsend A R, Erisman J W, Bekunda M, Cai Z, Freney J R, Martinelli L A, Seitzinger S P and Sutton M A 2008 Transformation of the nitrogen cycle: recent trends, questions, and potential solutions *Science* **320** 889

Goodale C L, Aber J D and Vitousek P M 2003 An unexpected nitrate decline in New Hampshire streams *Ecosystems* **6** 75–86

Helsel D R 2005 *Nondetects and Data Analysis* (New York: Wiley-Interscience)

Hirsch R M, Slack J R and Smith R A 1982 Techniques of trend analysis for monthly water quality data *Water Resources Res.* **18** 107–21

Howarth R W, Boyer E W, Pabich W J and Galloway J N 2002 Nitrogen use in the United States from 1961–2000 and potential future trends *AMBIO* **31** 88–96

Johnson H O, Gupta S C, Vecchia A V and Zvomuya F 2009 Assessment of water quality trends in the Minnesota River using non-parametric and parametric methods *J. Environ. Qual.* **38** 1018–30

Lettenmaier D P, Hooper E R, Wagoner C and Faris K B 1991 Trends in stream quality in the continental United States, 1978–87 *Water Resources Res.* **27** 327–39

Likens G E and Bormann F H 1995 *Biogeochemistry of a Forested Ecosystem* (New York: Springer)

Lins H F and Slack J R 1999 Streamflow trends in the United States *Geophys. Res. Lett.* **26** 227–30

Mann H B 1945 Nonparametric tests against trend *Econometrica* **13** 245–59

Milly P C D, Betancourt J, Falkenmark M, Hirsch R M, Kundzewicz Z W, Lettenmaier D P and Stouffer R J 2008 Stationarity is dead: whither water management? *Science* **319** 573–4

Peterjohn W T, Adams M B and Gilliam F S 1996 Symptoms of nitrogen saturation in two central Appalachian hardwood forest ecosystems *Biogeochemistry* **35** 507–22

Pielke R A Jr and Downton M W 2000 Precipitation and damaging floods: trends in the United States, 1932–97 *J. Clim.* **13** 3625–37

Rhoades C C *et al* 2013 Biogeochemistry of beetle-killed forest: explaining a weak nitrate response *Proc. Natl Acad. Sci. USA* **110** 1756–60

Richards R P and Baker D B 1993 Trends in nutrient and suspended sediment concentrations in Lake Erie tributaries, 1975–1990 *J. Great Lakes Res.* **19** 200–11

Rupert M G 2008 Decadal-scale changes of nitrate in ground water of the United States, 1988–2004 *J. Environ. Qual.* **37** 240–8

Sen P K 1968 Estimates of the regression coefficient based on Kendall's tau *J. Am. Stat. Assoc.* **63** 1379–89

Smith R A, Alexander R B and Wolman M G 1987 Water-quality trends in the nation's rivers *Science* **235** 1607–15

Sprague L A, Hirsch R M and Aulenbach B T 2011 Nitrate in the Mississippi River and its tributaries, 1980–2008: are we making progress? *Environ. Sci. Technol.* **45** 7209–16

Sprague L A, Mueller D K, Schwarz G E and Lorenz D L 2009 *Nutrient Trends in Streams and Rivers of the United States, 1993–2003* (*US Geological Survey Scientific Investigations Report* 2008–5202) (Reston, VA: USGS)

Stoddard J L 1994 Long-term changes in watershed retention of nitrogen, its causes and aquatic consequences *Environmental Chemistry of Lakes and Reservoirs* (*Advances in Chemistry Series* no 237) ed L A Baker (Washington, DC: American Chemical Society) pp 223–84

Swank W T and Vose J M 1997 Long-term nitrogen dynamics of Coweeta forested watersheds in the southeastern United States of America *Glob. Biogeochem. Cycles* **11** 657–71

Vitousek P M 1977 The regulation of element concentrations in mountain streams in the northeastern United States *Ecol. Monogr.* **47** 65–87

Vitousek P M and Reiners W A 1975 Ecosystem succession and nutrient retention: a hypothesis *BioScience* **25** 376–81