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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

 Online supplementary data available from stacks.iop.org/ERL/8/014039/mmedia

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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 ($\text{NO}_3\text{-N}$) and ammonium ($\text{NH}_4\text{-N}$) 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 $(x_1, y_1), (x_2, y_2), \dots, (x_n, y_n)$ 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:

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

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

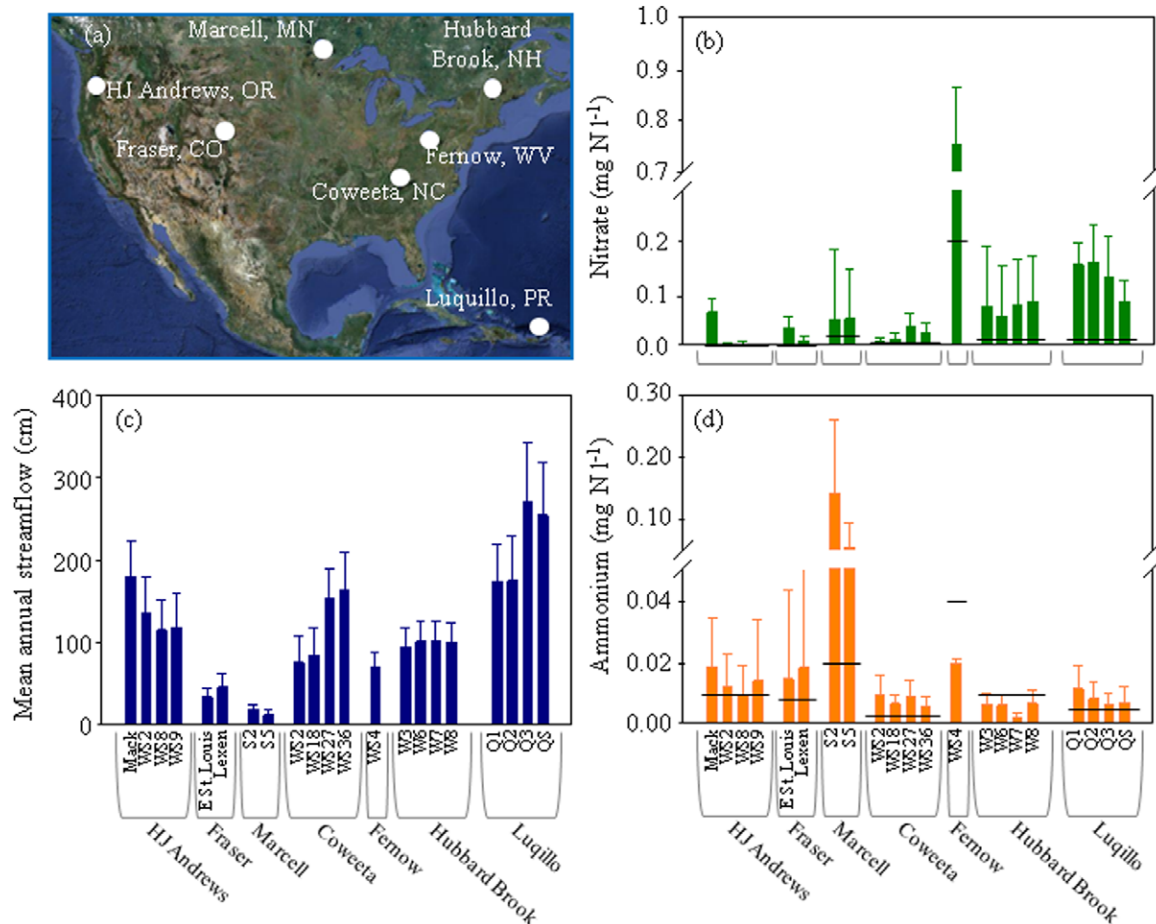


Figure 1. (a) Locations of the Experimental Forests included in this study; averages from 1996 to 2007 are shown for (b) mean monthly flow-weighted stream nitrate concentration, (c) mean annual streamflow, and (d) mean monthly flow-weighted stream ammonium concentration in study catchments. Error bars 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 ≤ 0.16 mg $\text{NO}_3\text{-N l}^{-1}$; average nitrate at Fernow was 0.75 mg

Site	Catchment	Trends in stream nitrate			Trends in stream ammonium			Trends in streamflow			Trends in nitrate concentration in wet deposition			Trends in ammonium concentration in wet deposition		
		1996-07 (12 yr)	1987-07 (21 yr)	1972-07 (36 yr)	1996-07 (12 yr)	1987-07 (21 yr)	1972-07 (36 yr)	1996-07 (12 yr)	1987-07 (21 yr)	1972-07 (36 yr)	1996-07 (12 yr)	1987-07 (21 yr)	1978-07 (30 yr)	1996-07 (12 yr)	1987-07 (21 yr)	1978-07 (30 yr)
HJ Andrews	Mack															
	WS2															
	WS8 WS9															
Fraser ¹	E St. Louis Lexen															
Marcell ²	S2															
	S5															
Coweeta	WS2															
	WS18															
	WS27															
	WS36															
Fernow	WS4															
Hubbard Brook	W3															
	W6															
	W7															
	W8															
	W9															
Luquillo	Q1	*			§			*								
	Q2	*			§			*								
	Q3	*			§			*								
	Q4	*			§			*								
	QS	*			§			*								
Increasing trends		6 (27.3%)	4 (23.5%)	4 (50.0%)	4 (18.2%)	4 (30.8%)	5 (62.5%)	0 (0.0%)	0 (0.0%)	0 (0.0%)	0 (0.0%)	0 (0.0%)	1 (16.7%)	2 (28.6%)	2 (28.6%)	3 (33.3%)
No trends		5 (22.7%)	6 (35.3%)	0 (0.0%)	9 (40.9%)	3 (23.1%)	1 (12.5%)	15 (68.2%)	14 (82.4%)	3 (37.5%)	5 (71.4%)	5 (71.4%)	1 (16.7%)	5 (71.4%)	4 (57.1%)	3 (50.0%)
Decreasing trends		11 (50.0%)	7 (41.2%)	4 (50.0%)	9 (40.9%)	6 (46.2%)	2 (25.0%)	7 (31.8%)	3 (17.6%)	5 (62.5%)	2 (28.6%)	2 (28.6%)	4 (66.7%)	0 (0.0%)	1 (14.3%)	1 (16.7%)

¹May to October, ²April, May, June, July, October, ³Period of 1997-2007, ⁴Period of 1989-2007, ⁵Period of 1980-2007, ⁶Period of 1998-2007, ⁷Period of 1985-2007

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.

NO₃-N 1⁻¹ (figure 1(b)). Ammonium concentrations in streams were equal to or below 0.01 mg NH₄-N 1⁻¹ at 19 of the 21 study catchments; concentrations higher than 0.01 mg NH₄-N 1⁻¹ were observed at Marcell (0.14 mg NH₄-N 1⁻¹ at S2 and 0.05 mg NH₄-N 1⁻¹ 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 NO₃-N 1⁻¹ 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 NH₄-N 1⁻¹ 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

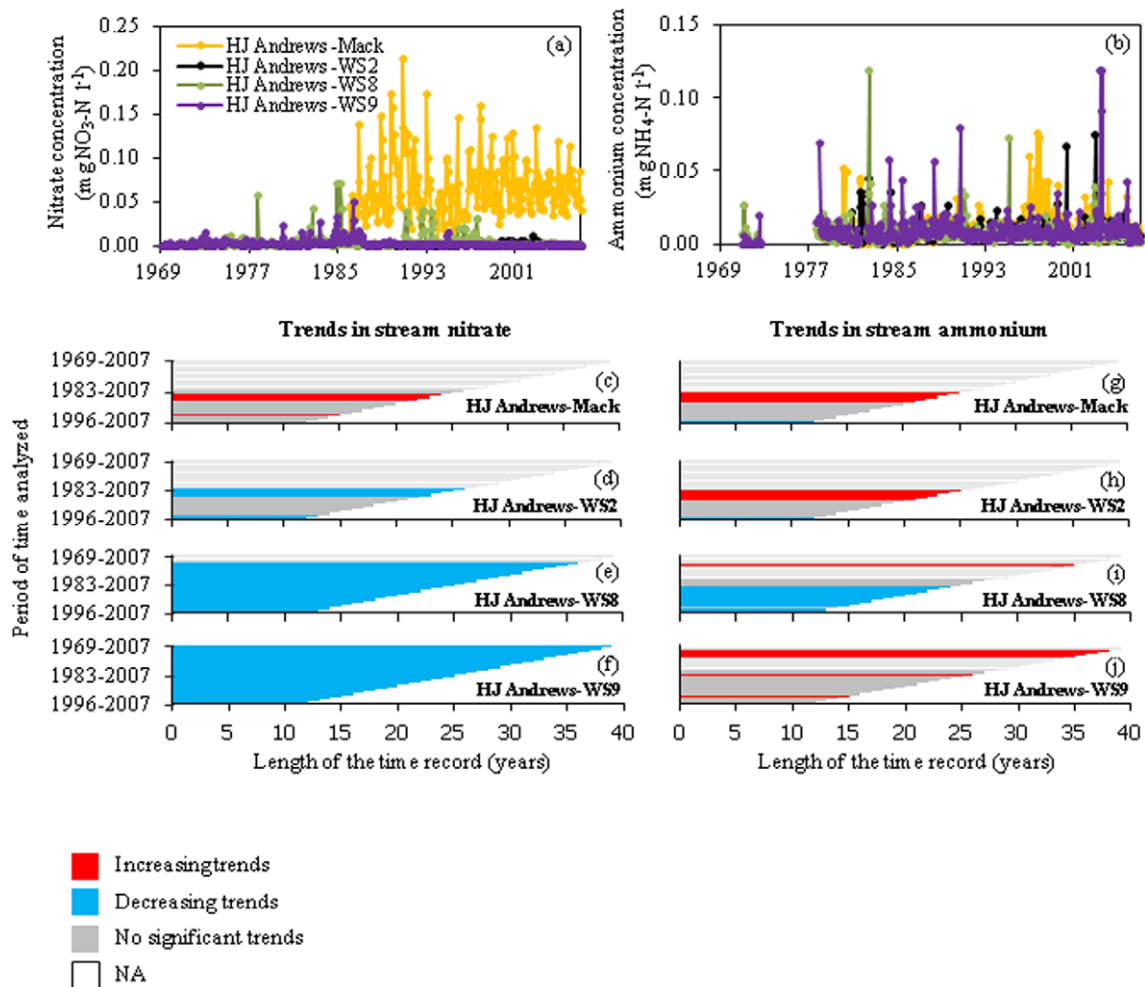


Figure 3. Mean monthly flow-weighted (a) stream nitrate and (b) stream ammonium concentrations at HJ Andrews and trends in (c)–(f) nitrate and (g)–(j) ammonium concentrations at four HJ Andrews catchments. Trends are calculated for the recent 12 yr and then for longer periods by adding successive 1 yr 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 $8.2 \mu\text{g NO}_3\text{-N l}^{-1} \text{ yr}^{-1}$) 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 $40.0 \mu\text{g NO}_3\text{-N l}^{-1} \text{ yr}^{-1}$). 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 $0.3 \mu\text{g NO}_3\text{-N l}^{-1} \text{ yr}^{-1}$ while increases of 1.6 and $0.8 \mu\text{g NO}_3\text{-N l}^{-1} \text{ yr}^{-1}$ 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 ($-4\% \text{ yr}^{-1}$, $-2\% \text{ yr}^{-1}$, $4\% \text{ yr}^{-1}$ and $3\% \text{ yr}^{-1}$ 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 $0 \mu\text{g N l}^{-1} \text{ yr}^{-1}$ 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.

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

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SUPPLEMENTARY MATERIAL

S1. Site characterization

The **HJ Andrews Experimental Forest** is situated in the western Cascade Range of Oregon, USA, in the 6400-ha drainage catchment of Lookout Creek (Lat 44° 14' N Long 122° 10' W, figure 1a). Elevation ranges from 410 m to 1630 m. The climate at the HJ Andrews is cool and wet in winter and warm and dry in summer. Mean monthly air temperature is 1°C in January and 18°C in July. Annual precipitation averages 213 cm at low elevation, with higher amounts at higher elevations; majority of precipitation falls between October and March as rain at low elevations and as rain and snow at upper elevations. Soil temperatures generally remain above freezing. We used data from 4 reference catchments: WS9 is smallest (8.5 ha) and has its gage at the lowest elevation, WS8 is also small (21.4 ha) and is at the highest elevation, WS2 is approx. 60 ha and Mack Creek is 581 ha. Mack Creek catchment had several small harvests in upper elevation between 1957 and 1982 that total 12% of area. Forest age classes in reference catchments are 200- and 550-year-old stands developed after wildfire. Vegetation is dominated by Douglas-fir (*Pseudotsuga menziesii*), and western hemlock (*Tsuga heterophylla*) forests.

The **Fraser Experimental Forest** is located within the Arapaho-Roosevelt National Forest, 81 km northwest of Denver, Colorado, USA (Lat 39° 54' N Long 105° 53' W, figure 1a). The elevation at Fraser ranges from 2650 to 3900 m. The mean annual temperature is 1°C, ranging between -40°C and 32°C annually. Annual precipitation averages 58 cm at the Headquarters wet deposition collection station and averages 74 cm over the entire research forest with two-thirds falling as snow (Alexander and Watkins 1977). Lodgepole pine (*Pinus contorta* var. *latifolia* Engelm. ex Wats.) stands dominate the lower elevations and southern aspects. Mixed-species forests of subalpine fir (*Abies lasiocarpa* (Hook.) Nutt.), Engelmann spruce (*Picea engelmannii* Parry ex Engelm.) and lodgepole pine occupy valley bottoms and north-facing slopes and extend to treeline (3300–3500 m). Quaking aspen (*Populus tremuloides* Michx.) occurs in small clonal stands, scattered throughout the lower elevations. We used

data from 2 reference catchments, East St Louis (802.9 ha) and Lexen (123.8 ha). Mountain pine bark beetle (*Dendroctonus ponderosae* Hopkins) began to cause widespread, lodgepole pine mortality at Fraser in 2002 (Tishmack *et al* 2004). As of 2010, ~40% of total overstory basal area or 75% of pine basal area had been killed in many stands at Fraser (Collins *et al* 2011).

The **Marcell Experimental Forest** is located in north central Minnesota, USA (Lat 47° 32' N Long 93° 28' W, figure 1a) along the continental divide of the Mississippi River and Hudson Bay drainages. The glacial terrain has subtle topography with topographic relief that is less than 20 m in each of six research catchments; there is no dominant aspect. In each research catchment, upland mineral soils drain through one or more central peatlands to an outlet stream. We used data from 2 reference catchments, S2 (9.7 ha) and S5 (52.6 ha). The climate is continental with a mean monthly air temperature of 19 °C during July and -15°C during January. The growing season is June through September, and mean annual precipitation is 78 cm. Vegetation types are conifer, aspen-birch, or mixed northern hardwoods on upland soils. Most upland forest regeneration dates from the mid-1910s when forests throughout the area were clearcut. Black spruce (*Picea mariana*), larch (*Larix laricina*), ericaceous shrubs, and *Sphagnum* dominate deep organic soils on ombrotrophic bogs in the peatlands; most peatland forests are at least 150 years old.

The **Coweeta Hydrologic Laboratory** is located in the southern Appalachian Mountains of western North Carolina, USA (Lat 35° 00' N Long 83° 30' W, figure 1a). We used data from 4 reference catchments with areas ranging between 12 and 49 ha: WS2 (12.3 ha), WS18 (12.5 ha), WS27 (39 ha), and WS36 (48.6 ha). The climate is marine, humid temperate (Adams *et al* 2004) with highest temperatures between June and August (20°C) and lowest between December and January (-5°C). The growing season extends from early May to early October and annual precipitation is 190 cm (>10 cm in most months). The major vegetation community types at Coweeta include in order of dominance: mesic mixed oak, northern hardwoods, cove hardwoods, and dry mixed-oak pine vegetation community types. Natural disturbances between 1970 and 2007 include a fall cankerworm infestation from 1972 to 1979 which partially defoliated WS27 and WS36, and a major drought across the southeast between 1985 and 1988, with a peak year in 1986 as described in Vose and Swank (1994), a severe drought in 1998, 2000, 2001, and 2006 with the lowest rainfall on record in 2007. Hurricane impacts include Opal in Oct 1995, and Francis and Ivan in Sep 2004.

The **Fernow Experimental Forest** is located in north-central West Virginia in the Allegheny Mountain section of the mixed mesophytic forest (Lat 39° 03' N Long 79° 41' W, figure 1a). We used data from WS4 (39 ha), which has remained undisturbed since approximately 1905. The climate is humid continental, with mean monthly temperatures of -18°C in January and 21°C in July during the 1996-2007 period. The growing season extends from May through October, and the average length of the frost free season is 145 days (Adams and Kochenderfer 2007). Annual precipitation averages 146 cm and it is evenly distributed throughout the year. During winter, precipitation occurs often in the form of snow, but a seasonal snow pack (and spring melt event) does not usually occur. The site includes mixed hardwood forests with yellow-poplar (*Liriodendron tulipifera* L.), sugar maple (*Acer saccharum* Marsh.), black cherry (*Prunus serotina* Ehrh.), red oak (*Quercus rubra* L.) and basswood (*Tilia americana* L.). The most common natural disturbances are high rainfall events (e.g. in 1972, 1975, and 1985) and windstorms (e.g., 1993 and 1998, Adams *et al* 2003).

The **Hubbard Brook Experimental Forest** is located in the White Mountain National Forest of central New Hampshire (Lat 43° 56' N Long 71° 45' W, figure 1a). We used data from 5 catchments

within the site: W3 (42.4 ha), W6 (13.2 ha), W7 (76.4 ha), W8 (59.4 ha), and W9 (68.2 ha). The climate is humid continental with contrasting temperatures between winter (average January temperature is -9°C) and summer (average July temperature is 18°C). The average length of the frost free season is 145 days. Annual precipitation at Hubbard Brook averages 140 cm, with one-third to one-quarter as snow, and it is distributed throughout the year (Bailey *et al* 2003). Vegetation is characterized by northern hardwood forests dominated by sugar maple (*Acer saccharum* Marsh.), American beech (*Fagus grandifolia* Ehrh.), and yellow birch (*Betula alleghaniensis* Britt). Balsam fir (*Abies balsamea* (L.) Mill.) and red spruce (*Picea rubens* Sarg.) are found primarily at higher elevations, particularly on north-facing slopes (Likens and Bormann 1995). Hubbard Brook catchments have been affected by disturbances including heavy logging between 1905 and 1917, a hurricane in 1938 and subsequent salvage logging, a severe drought in 1963-64, a soil freezing event in 1989, and an ice storm in 1998.

The **Luquillo Experimental Forest** is located in the Luquillo Mountains of northeastern Puerto Rico (Lat 18° 15' N Long 65° 45' W, figure 1a). We used data from 4 catchments within the site: QS (265 ha), Q1 (6.7 ha), Q2 (6.3 ha), and Q3 (35 ha). The site is characterized by a tropical rainforest climate with annual average temperatures c. 22°C and little seasonality. Mean annual rainfall ranges from 340 to 424 cm (Garcia-Martino *et al* 1996) and it is distributed throughout the year, however a drier period typically occurs between February and April, and a wetter period occurs from September to December. Dominant vegetation includes tabonuco, colorado, and elfin forests at progressively higher elevations, with sierra palm forests concentrated along streams (Brown *et al* 1983). Luquillo catchments have been affected by hurricanes Hugo (1989), Hortense (1996), and Georges (1998), and drought (Feb 1993 to Aug 1994).

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Supplementary material: Nitrogen Trends In Reference Catchments

Garcia-Martino A R, Warner G S, Scatena F N, and Civco D L 1996 Rainfall, runoff and elevation relationships in the Luquillo Mountains of Puerto Rico *Caribbean Journal of Science* **32**: 413-24

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Table S1. Mean annual values for climatic variables for the period of 1996-2007.

Experimental Forest	Location	DIN record start ¹	Mean annual precipitation (cm)	Mean annual streamflow ² (cm)	Min and max air temp (temp range) ³ (°C)	Mean annual dissolved inorganic N in wet deposition (kg ha ⁻¹)	Dominant vegetation	Dominant geology
HJ Andrews	Willamette National Forest, OR	1968	225	136	4.2 to 16.8 (12.6)	0.9	Douglas-fir, western hemlock	Volcanic, andesite
Fraser	Arapaho-Roosevelt National Forest, CO	1984	60	38	-6.7 to 10.2 (16.9)	2.5	Subalpine forest, alpine tundra	Metamorphic schist, gneiss
Marcell	Chippewa National Forest, MN	1970	76	14	-2.3 to 10.6 (12.9)	3.8	Forested peatlands, upland mixed northern hardwoods and conifers	Deep outwash sands (>50m) with a glacial till cap over Precambrian greenstone
Coweeta	Nantahala National Forest, NC	1971	171	118	6.9 to 20.6 (13.7)	4.3	Mixed oak hardwood, northern hardwood, and cove hardwoods	Metasandstone, schist
Fernow	Monongahela National Forest, WV	1980	146	69	3.8 to 14.5 (10.7)	5.6	Mixed mesophytic hardwoods	Sandstone, shale
Hubbard Brook	White Mountain National Forest, NH	1964	143	98	1.6 to 11.0 (9.4)	4.6	Northern hardwoods	Glacial till over schist, quartzite
Luquillo	El Yunque National Forest, PR	1983	390	218	21.2 to 26.9 (5.7)	2.8	Evergreen broadleaf tropical forest	Late Cretaceous igneous rock with Tertiary intrusives

¹Dissolved inorganic nitrogen²Mean of mean annual streamflow of all catchments of the site considered in this study³Mean of the monthly absolute minimum and maximum temperature

S2. Details of analytical procedures and sampling of stream chemistry

Calculation of flow-weighted concentrations: We used mean monthly flow-weighted concentrations in the analysis of trends to allow comparison among sites having different sampling histories. We calculated flow-weighted concentrations for Luquillo, Fernow, Marcell, and Fraser. Chemistry samples that were collected less than 16 days apart were linearly interpolated to estimate a daily concentration, which was then multiplied by the total daily streamflow to calculate total daily flux. The total daily flux was summed over the month and then was divided by the monthly accumulated streamflow to obtain monthly flow-weighted concentrations. Hubbard Brook, Coweeta, and HJ Andrews calculated monthly flow-weighted concentrations and shared those data. For Hubbard Brook, solute concentrations between adjacent sampling times were averaged and multiplied by daily streamflow. For Coweeta, the value of the sampling day was used for the period between the sampling day and the previous sampling day. Monthly flow-weighted concentrations at HJ Andrews were calculated using concentrations from 2 or 3 three-week composite samples. Samples that extended across months were subset using daily flows in order to have weighted concentrations for each month.

Data: Stream chemistry data were obtained from the individual EFRs. Streamflow data were obtained from the Climate and Hydrology Database Projects (ClimDB/HydroDB; <http://www.fsl.orst.edu/climhy>) and from the individual EFRs. Precipitation chemistry data were obtained as wet deposition chemistry from the National Atmospheric Deposition Program (NADP; <http://nadp.sws.uiuc.edu/>) for all sites except Fraser, where data were obtained directly from the site.

Table S2. Details of analytical procedures, statistical methods, and sampling of stream chemistry.

Site	Sample frequency, method	Sample procedures and storage	Nitrate analysis method (analyte measured)	Ammonium analysis method	Detection limits used in the analysis of the longest period of time	References ^a
HJ Andrews	3-week composites	Samples composite over a 3 week period and collected at a rate proportional to streamflow. Stored in an insulated carboy at each gaging station and refrigerated each week. Filtered after arriving at the lab and analyzed within 2 days.	Colorimetric, automated Cd-Cu reduction method –manual before 1980- (NO ₃ -N + NO ₂ -N)	Colorimetric. Prior to 1980: Nesslerization; After 1980: Technicon Auto-analyzer II	0.001 mg NO ₃ -N L ⁻¹ ; 0.010 mg NH ₄ -N L ⁻¹	Martin and Harr 1988
Fraser	Weekly (April to October), grab	Water samples are filtered and cooled until analysis.	Ion chromatography (NO ₃ -N)	Ion chromatography	0.002 mg NO ₃ -N L ⁻¹ ; 0.010 mg NH ₄ -N L ⁻¹	
Marcell	Biweekly (April to October), grab	Water chemistry is measured on unfiltered water samples that have been chilled until analysis.	Colorimetric, automated Cd-Cu reduction method (NO ₃ -N + NO ₂ -N)	Flow-injection analysis: Colorimetric, Alkaline phenol method	0.020 mg NO ₃ -N L ⁻¹ ; 0.020 mg NH ₄ -N L ⁻¹	Sebestyen <i>et al</i> 2011
Coweeta	Weekly, grab	Water samples are analyzed within 2 days of collection. If samples must be stored, they are frozen until analyzed.	Prior to June 1990: colorimetric, automated Cd-Cu reduction method (NO ₃ -N + NO ₂ -N); Since July 1990: ion chromatography (NO ₃ -N)	Colorimetric, Alkaline phenol method	0.001 mg NO ₃ -N L ⁻¹ ; 0.002 mg NH ₄ -N L ⁻¹	
Fernow	At least biweekly, grab	Samples are transported to the lab where they are filtered, split, and stored cool until analysis.	Prior to 1981: colorimetric, Hach method, NitraVer IV; Since 1981: ion chromatography (NO ₃ -N)	Prior to 1981: Wescan NH ₄ analyzer; Since 1981: ion chromatography	0.219 mg NO ₃ -N L ⁻¹ (IDL), 0.040 mg NH ₄ -N L ⁻¹	Edwards and Wood 1993
Hubbard Brook	Weekly, grab	Samples are unfiltered and not preserved prior to analysis. Sent to Cary Institute of Ecosystem Studies, Millbrook, NY for chemical analyses.	Prior to 1970: spectrophotometric, phenoldisulfonic acid technique; 1970-76: colorimetric, automated Cd-Cu reduction method (NO ₃ -N + NO ₂ -N); 1977-present: ion chromatography (NO ₃ -N)	Prior to 1970: spectrophotometric, using Nessler's reagent; 1970-present: colorimetric, automated indophenol-blue method	0.004 mg NO ₃ -N L ⁻¹ , 0.016 mg NH ₄ -N L ⁻¹	Buso <i>et al</i> 2000

Luquillo	Weekly, grab	1983-1994: Water samples filtered and cooled until analysis. Subsamples for NH ₄ were also preserved with 1M H ₂ SO ₄ . Since 1994: samples filtered and frozen until analysis, not acidified.	Prior to Sept. 1989: colorimetric, automated Cd-Cu reduction method (NO ₃ -N + NO ₂ -N); Sept. 1989 to present: liquid chromatography with UV or conductivity detection (NO ₃ -N)	1983 to present: colorimetric, automated, phenol hypochlorite method	0.010 mg NO ₃ -N L ⁻¹ , 0.005 mg NH ₄ -N L ⁻¹	Schaefer <i>et al</i> 2000
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^a References:

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S3. Results of the Sen’s estimator of the slope

Site	Catchment	Trends in stream nitrate and slope of the trend (µg N L ⁻¹ yr ⁻¹)			Trends in stream ammonium and slope of the trend (µg N L ⁻¹ yr ⁻¹)			Trends in streamflow and slope of the trend (mm yr ⁻¹)			Trends in nitrate in wet deposition and slope of the trend (µg N L ⁻¹ yr ⁻¹)			Trends in ammonium in wet deposition and slope of the trend (µg N L ⁻¹ yr ⁻¹)		
		1996-07 (12 ys)	1987-07 (21 ys)	1972-07 (36 ys)	1996-07 (12 ys)	1987-07 (21 ys)	1972-07 (36 ys)	1996-07 (12 ys)	1987-07 (21 ys)	1972-07 (36 ys)	1996-07 (12 ys)	1987-07 (21 ys)	1978-07 (30 ys)	1996-07 (12 ys)	1987-07 (21 ys)	1978-07 (30 ys)
HJ Andrews	Mack	0.3	0.4		-0.8	0.1		-1.0	0.1		-0.5	-0.9	0.0 [§]	0.0	0.0	0.0 [§]
	WS2	0.0	0.0		-0.3	0.0		-0.9	0.2							
	WS8	-0.3	-0.1	0.0	-0.1	-0.1	0.0	-0.6	0.1	-0.1						
	WS9	0.0	0.0	0.0	0.0	0.0	0.1	-0.8	-0.8	-0.3						
Fraser ¹	E St. Louis	2.3	0.8		0.0	0.0		-0.8	0.0		-4.4	-1.6		0.0	2.1	
	Lexen	0.5	0.2		0.0	0.0		-1.7	0.0							
Marcell ²	S2	-1.2			1.4			-0.7			-11.3	-7.2	-6.4	16.8	10.0	2.9
	S5	-0.3			-1.4			-0.4								
Coweeta	WS2	-0.3	0.0	0.1	0.4	0.3	0.1	-1.2	-0.5	-0.3	-3.7	-4.0	-3.8	5.7	2.7	1.4
	WS18	-0.3	0.0	0.1	0.3	0.2	0.1	-1.6	-0.6	-0.6						
	WS27	1.6	0.8	0.3	0.8	0.3	0.1	-3.3	-1.0	-0.8						
	WS36	0.8	0.7	0.4	0.5	0.2	0.0	-3.5	-1.4	-0.6						
Fernow	WS4	8.2	1.7		0.0	0.0		-0.4	0.2		-50.0	-40.0	-26.4	0.0	0.0	0.0
Hubbard Brook	W3	-1.0	-1.0	-4.5	0.0	-0.6	-0.3	0.0	0.2	0.0	-62.5	-34.0	-26.3	0.0	0.0	0.0
	W6	0.0	-0.5	-4.2	0.0	-0.7	-0.3	0.0	0.4	0.1						
	W7	0.2			0.0			-0.4								
	W8	-0.3			0.0			0.0								
	W9	0.3			0.0			-0.4								
Luquillo	Q1	-4.6 [*]	1.0		-0.3 [§]			2.3 [*]	0.6		0.0	2.0	6.0 [♠]	0.0	0.0	0.0 [♠]
	Q2	-10.0 [*]	-4.0		-0.3 [§]			-2.0 [*]	-0.7							
	Q3	-8.5 [*]	-4.3		0.0 [§]			6.2 [*]	0.7							
	QS	-4.8 [*]	-2.7		0.0 [§]			4.5 [*]	0.9							

¹May to October, ²April, May, June, July, October [§]1980-2007, [♠]1985-2007, ^{*}1997-2007, [°]1998-2007

Figure S1. Results of the Sen’s estimator of the slope and 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, grey denotes no significant trends, and blue denotes decreasing trends for that period of time and catchment.

S4. Stream nitrate concentration vs. time for all sites

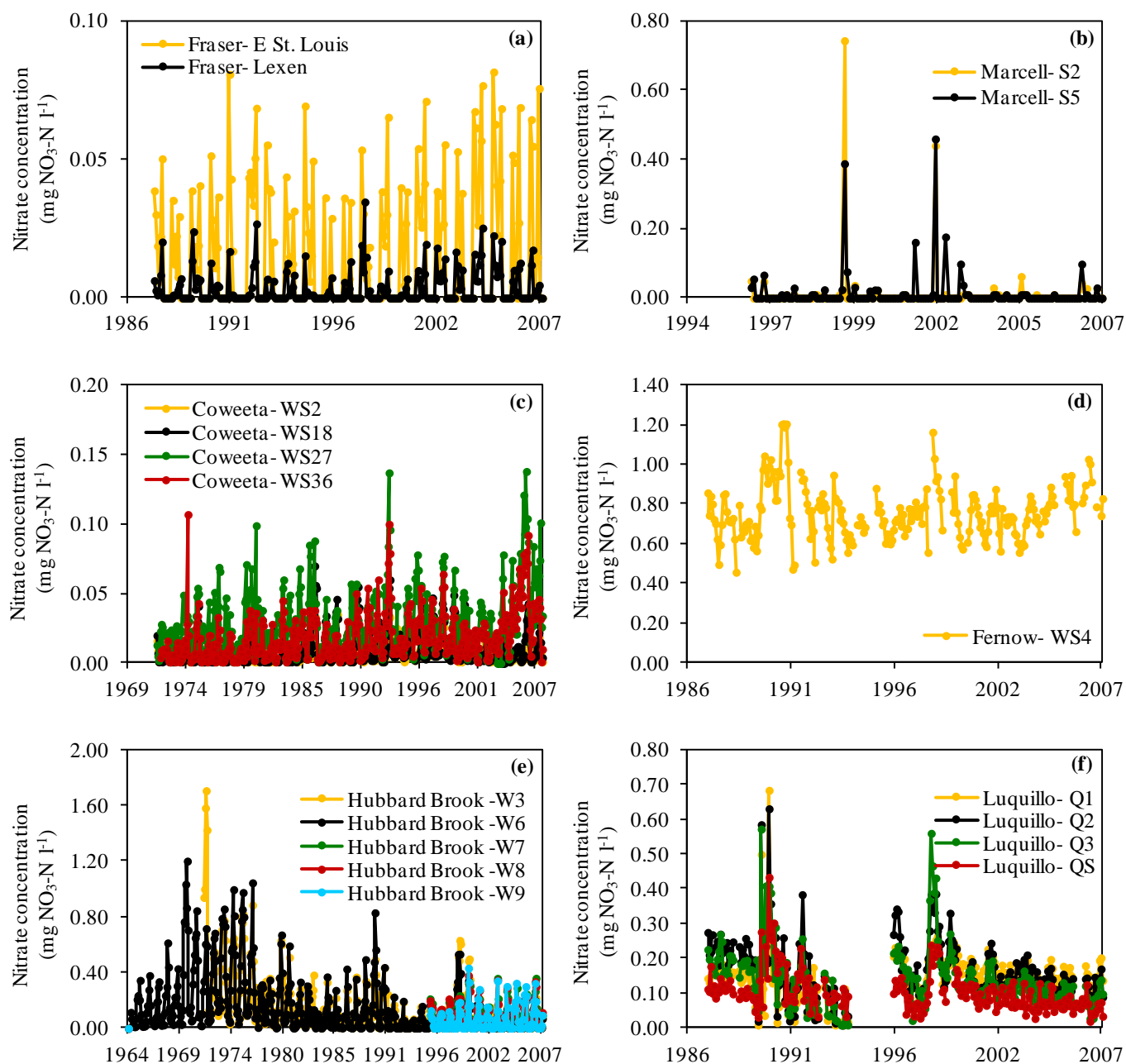


Figure S2 .Mean monthly flow-weighted stream nitrate vs. time at (a) Fraser Experimental Forest, (b) Marcell Experimental Forest, (c) Coweeta Hydrologic Laboratory, (d) Fernow Experimental Forest, (e) Hubbard Brook Experimental Forest, and (f) Luquillo Experimental Forest.

Cont. S4. Stream nitrate concentration vs. time for all sites

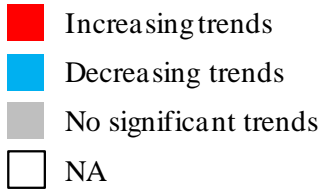
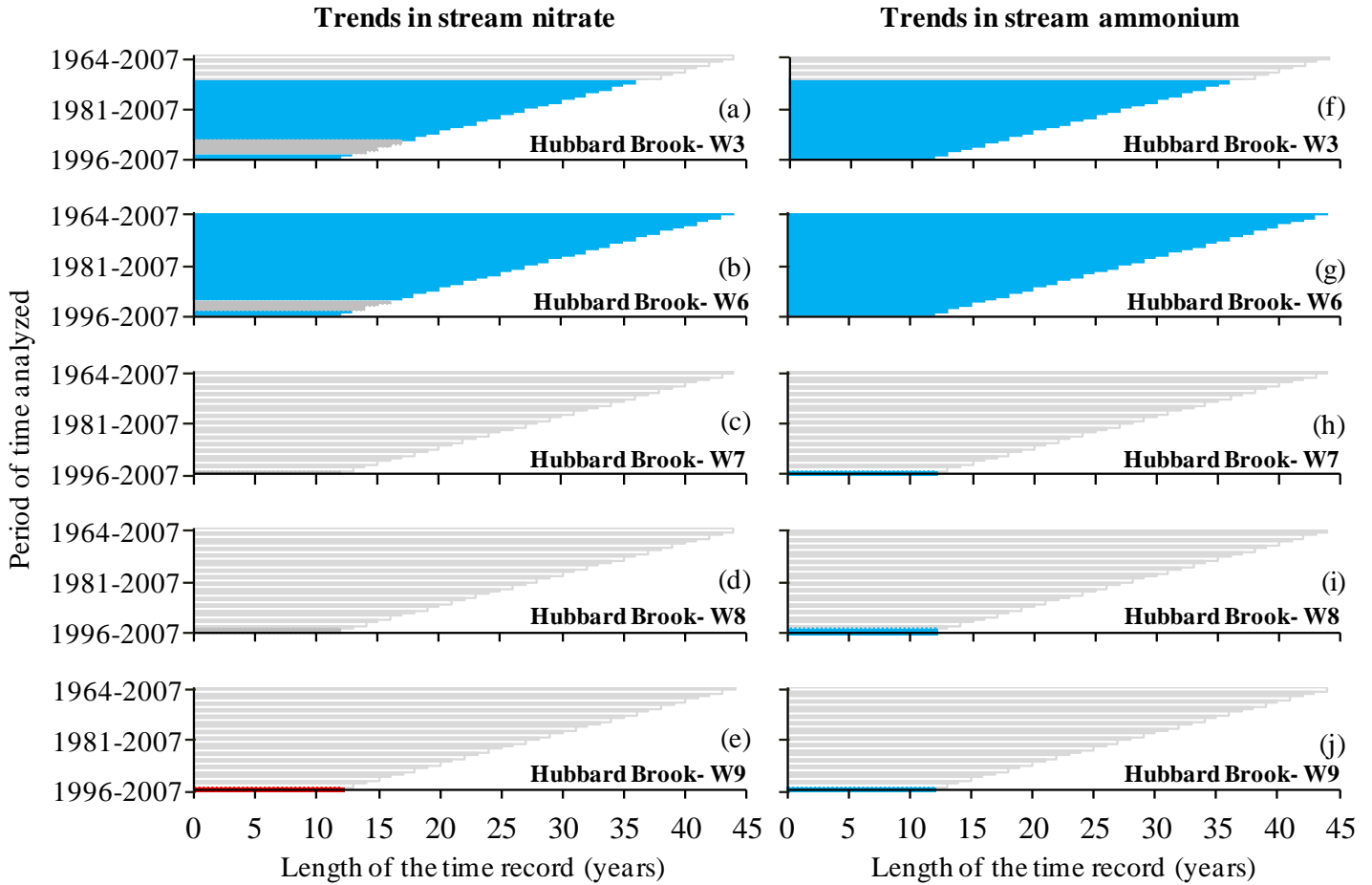


Figure S3 .Trends in stream nitrate (a-e) and ammonium (f-j) concentration at five Hubbard Brook reference catchments.

S5. Data source citation and acknowledgements

Hydrology and climate data were downloaded through Climate and Hydrology Database Projects (Hydro/ClimDB; <http://www.fsl.orst.edu/climhy>), a partnership between the Long-Term Ecological Research program and the U.S. Forest Service.

Ammonium and nitrate concentration in atmospheric wet deposition data were obtained from the National Atmospheric Deposition Program (NRSP-3). 2011. NADP Program Office, Illinois State Water Survey, 2204 Griffith Dr., Champaign, IL 61820. [Database] <http://nadp.sws.uiuc.edu/educ/> (Downloaded Oct 2010). Note that the data used in this paper (atmospheric wet deposition) is different than bulk precipitation data reported in numerous, long-term studies published at Hubbard Brook.

HJ Andrews: Data were provided by the HJ Andrews Experimental Forest research program, funded by the National Science Foundation Long Term Ecological Research program (DEB 08-23380), the US Forest Service Pacific Northwest Research Station, and Oregon State University.

Johnson SL and Fredriksen R. 2010. Stream chemistry concentrations and fluxes using proportional sampling in the Andrews Experimental Forest, 1968 to present. Long-Term Ecological Research. Forest Science Data Bank, Corvallis, OR.

<http://andrewsforest.oregonstate.edu/data/abstract.cfm?dbcode=CF0002> (Downloaded: 1/Nov/10).

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<http://andrewsforest.oregonstate.edu/data/abstract.cfm?dbcode=HF004> (Downloaded: 12/Jan/11).

Fraser: Stream nitrogen, wetfall deposition and streamflow data were provided by the US Forest Service Rocky Mountain Research Station, Fraser Experimental Forest. Streamflow data are available at: <http://www.fs.usda.gov/main/fraser/data>. R. Stottleyer designed and directed chemistry sampling and analysis for the Fraser Experimental Forest from its inception until 2003.

Marcell: Current streamflow and precipitation metadata and data can be found at: <http://nrs.fs.fed.us/ef/marcell/data/>.

Sebestyen, S. D., C. Dorrance, D. M. Olson, E. S. Verry, R. K. Kolka, A. E. Elling, and R. Kyllander (2011), Long-term monitoring sites and trends at the Marcell Experimental Forest, in Peatland biogeochemistry and watershed hydrology at the Marcell Experimental Forest, edited by R. K. Kolka, *et al*, pp. 15-71, CRC Press, Boca Raton, FL.

Coweeta Hydrologic Laboratory: Stream nitrogen and streamflow data were provided by the US Forest Service, Southern Research Station, Coweeta Hydrologic Laboratory. Collection, analysis, and maintenance of these data is funded by Southern Research Station, Forest Service, US Department of Agriculture, and National Science Foundation grant DEB-9632854 to the Coweeta Long-Term Ecological Research Program. Long-term climatic data and other datasets are available at: <http://www.srs.fs.usda.gov/coweeta/>.

Fernow: Current stream streamflow, chemistry, and precipitation databases can be found at: <http://www.fs.fed.us/ne/parsons/webdata/index.htm>. Some of the data were collected as part of the Fernow Watershed Acidification Study, which has been funded by the National Science Foundation's Long-Term Research in Environmental Biology program (since 2003), the US Environmental Protection Agency (1988-1990), and the USDA Forest Service Northern Research Station (1988 to present).

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Luquillo: Funding for data collection came from NSF LTER DEB-0620919, NSF OPUS DEB-0816727, NSF DEB-0108385, the USDA Forest Service International Institute of Tropical Forestry, and the University of Puerto Rico ITES. Particular thanks go to Jeff Merriam and John Bithorn for help in the laboratory and field. Data are available from <http://luq.lternet.edu/data/luqmetadata20>.