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Long-term monitoring of precipitation chemistry in the U.S.: Insights into changes and condition

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HIGHLIGHTS

- Acid rain discovered in North America in 1963.
- Increasing precipitation acidity in eastern North America from the 1950's to the 1970's, and decreasing thereafter.
- National maps clearly convey occurrence and trends of acid rain to the public and policy makers.
- Declines of 85%, 80% and 66% in H^+, SO_4^{2-}, and NO_3^- in precipitation chemistry from 1981 to 2017 in NE U.S.
- Comparable declines in sulfur and nitrate dry deposition.

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ABSTRACT

Continuous monitoring of precipitation chemistry began at the Hubbard Brook Experimental Forest, NH in June 1963, and it was there that acid rain was discovered in North America. Some independent monitoring of precipitation chemistry in central New York was done in 1970–1971. The MAP3S network (Charlottesville, VA, Ithaca, NY, Penn State, PA, Whiteface Mt., NY) began in 1976 and became part of the National Atmospheric Deposition Program (NADP) in 1992. Using data from these long-term sites, and other published information, we show the status and temporal change of precipitation chemistry in the northeastern U.S. from 1963 to present. Combining records from all stations and networks gave better insights into the status and temporal trends of precipitation chemistry for the region particularly as detailed regional maps could be constructed from these data. Early maps of predicted pH (1955-56 and 1965-66) and individually measured pH values (1975-76), as well as cartoons provided important visual information about the occurrence and spread of acid rain in the northeastern U.S. These indicators of changing atmospheric chemistry were key in initiating federal policy necessary for improving air quality and for reducing atmospheric pollutant loading, which had led to acid rain in this area, starting in the 1950s. Analyzing combined records from Hubbard Brook and the 5 longest operating MAP3S/AIRMoN sites (IL11, NY67, DE02, PA15 and TN00) with a random coefficient model showed overall declines in annual concentrations of H^+, SO_4^{2-} and NO_3^- from 1981 to 2017 of 85%, 80% and 66%, respectively. Calcium concentration declined by 14% and NH_4^+ showed no change during this period. Dry deposition of sulfur, NO_3^- and Ca^{2+} measured at co-located Clean Air Status and Trends Network (CASTNET) sites showed declines of 87%, 64% and <1%, respectively, during 2000–2017. As precipitation and air chemistry networks expanded to include the entire US (and Canada), dramatic improvements in precipitation chemistry nationwide, brought about by federal, clean air legislation, have been clearly documented.

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1. Introduction

Truly long-term records from high-quality monitoring efforts are rare, but they provide unique insights for evaluating environmental change and condition (Table 1). Characteristics of successful long-term monitoring are given in Table 2.

Continuous, comprehensive, long-term monitoring of precipitation chemistry started at the Hubbard Brook Experimental Forest (HBEF) in the White Mountains of NH in June 1963 as part of the Hubbard Brook Ecosystem Study (Bormann and Likens 1967, Likens, 2013; Holmes and Likens 2016). Starting in 1976, several other locations initiated long-term monitoring in the eastern U.S. as part of the Multi-State Atmospheric Power Production Pollution Study (MAP3S) network (MacCracken, 1978). In the United States, the National Atmospheric Deposition Program (NADP) began weekly wet-only sampling in 1978. This National Trends Network (NADP/NTN) now includes over 250 active sites (https://nadp.slh.wisc.edu/nadp/). In 1992, the MAP3S event, wet-only network became the daily NADP Atmospheric Integrated Research and Monitoring Network (NADP/AIRMoN) (https://nadp.slh.wisc.edu/AIRMoN/). The NADP/AIRMoN ceased operation in September 2019. The Canadian Air and Precipitation Monitoring Network (CAPMoN) began collecting wet-only daily precipitation samples in 1983, although two earlier Canadian networks began sampling precipitation chemistry in 1978 (http://data.ec.gc.ca/data/air/monitor/networks-and-studies/canadian-air-and-precipitation-monitoring-network-capmon/). The CAPMoN precipitation chemistry network in Canada now includes ~28 sites.

Acid rain was discovered at Hubbard Brook in 1963 (Likens et al., 1972) and was confirmed as a major environmental problem by ongoing monitoring at the Hubbard Brook site (e.g., Likens, 2013; Holmes and Likens 2016), at early sites in Ithaca and Aurora, NY (Likens 1972), and at various sites in the MAP3S network in the eastern U.S. Subsequent decades of monitoring precipitation chemistry at numerous sites showed the acidification and then recovery from acidification throughout eastern North America. Here, we present long-term data relevant to these significant changes in the atmospheric chemistry of the eastern U.S. as inferred from precipitation chemistry measured at several of these long-term sites (Fig. 1). Furthermore, long-term monitoring on a national scale has shown dramatic changes in precipitation chemistry, as well as wet and dry deposition, throughout the U.S.

1.1. Sites

The Hubbard Brook Ecosystem Study at the HBEF, NH, has been collecting and analyzing bulk precipitation chemistry continuously since June 1963. In addition, the HBEF became a NADP/NTN weekly, wet-only site (NH02) in 1978. Hubbard Brook became a National Dry Deposition Network (NDDN) site (WST 109) in 1988, which is now part of the Clean Air Status and Trends Network (CASTNET) (https://www3.epa.gov/castnet/site_pages/WST109.html). The NH02 and WST 109 sites are operational at about 250-m MSL elevation in the Hubbard Brook Valley, whereas the bulk precipitation sites are located at higher elevations (~600-m MSL) adjacent to the south-facing, experimental watersheds (Likens, 2013; Holmes and Likens 2016).

Starting in 1976, four sites (Whiteface Mt., NY – NY98, Ithaca, NY – NY67, Penn State, PA - PA15, and Charlottesville, VA – VA00) began collecting event precipitation samples as part of the MAP3S network. In November 1977, Illinois (IL11), in February 1978, Delaware (DE02) and in January 1981, Oak Ridge (TN00) were added to the network (Fig. 1; Supplemental Material, Part A). In 1992, NY67, PA15, IL11, DE02 and TN00 became part of the NADP daily sampling, AIRMoN Network. "Daily" samples were collected from the network when precipitation had occurred in the last 24 h, and were collected even when it was still precipitating. "Event" collection, which was the protocol for MAP3S, was defined as precipitation that occurred with no 6-h interval without precipitation. Previously, bulk precipitation chemistry was collected from two sites near NY67, at the Cornell University Game Farm Road in Ithaca, NY and the Cornell University Research Farm at Aurora, NY (Fig. 1) during 1970–1971 (Likens 1972).

In addition, four of the MAP3S/AIRMoN sites (PA15, NY67, IL11 and TN00) were co-located with the CASTNET (https://www.epa.gov/castnet) air quality and dry deposition monitoring network sites (PSU 106, CTH 110, BVL 130 and ONL 102, respectively).

Table 1
Some values of long-term data.

Identify and Quantify Extreme Events and Long-term Trends		
Evaluate Environmental Problems		
Quantitatively Evaluate Experimental Manipulations		
Establish Baselines for:		
Restoration Targets	Pristine Conditions	Federal and State Regulations

Table 2
What makes monitoring successful? (Adapted from Lindenmayer and Likens 2009, 2018).

Driven by good questions
Underpinned by a powerful and relevant conceptual model of system being monitorited
Based on a thoughtful experimental design, including valid statistical models
Collection of high-quality data and frequent referral to these data
Scientific productivity (use these data!)
Management relevance
Responsible (safe) storage of data and methodology, and robust data management

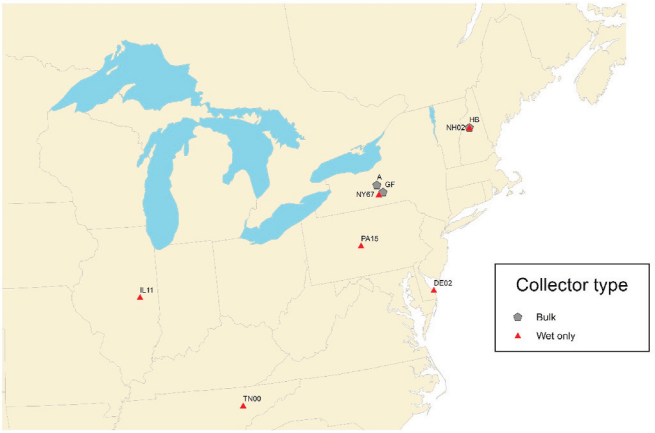

Fig. 1. Locations of major monitoring sites referred to in this study.

2. Methods

2.1. Hubbard Brook

Samples of rain and snow are collected with a continuously open, acid-washed, polyethylene funnel/bottle for rain and a polyethylene acid-washed, uncovered bucket for snow (bulk precipitation samples), at weekly intervals (Likens et al., 1967; Buso et al., 2000, Likens, 2013). Wet-only samplers are open to the atmosphere only when a precipitation event is occurring.

Volume-weighted averages (e.g. annual) are calculated by summing the amount of chemical from individual samples (e.g. weekly) and then dividing this value by the total amount of water during the period. Mass flux is calculated by multiplying the measured concentration of dissolved chemical in the accumulated composite sample of precipitation by the daily amounts of precipitation during the interval. The daily

values (g/ha-day) are summed to provide mass inputs by month or year (e.g. kg/ha-year). Chemical analyses were done by standard analytical procedures. Procedures were not changed during the long-term study unless the two procedures were overlapped for a year or more (Buso et al., 2000, Likens, 2013).

2.2. Ithaca, Aurora, NY67 and other MAP3S/AIRMoN long-term monitoring sites

Bulk samples from the Cornell University Game Farm Road site in Ithaca and the Cornell University Research Farm site in Aurora, NY, were collected and chemically analyzed in the same way as those from the Hubbard Brook bulk collectors. Protocols and quality control procedures for the MAP3S event samples are described in Dana (1988). The NADP/AIRMoN and NADP/NTN Standard Operating Procedures and Quality Assurance Reports are available at: (http://nadp.slh.wisc.edu/lib/).

Many of the long-term monitoring sites have additional research related to atmospheric deposition, particularly dry deposition (CASTNET), which compliments the continuous wet deposition record, and are co-located with many NADP sites. Sulfur species measured by CASTNET include gaseous SO_2 and particulate SO_4^{2-}. Nitrogen species include HNO_3, and particulate NO_3^- and NH_4^+. In addition, NADP biweekly NH_3 air concentrations have been monitored using passive samplers, at NY67 and IL11 since 2007 and a site near PA15 (PA96), which began in 2015 (http://nadp.slh.wisc.edu/data/sites/AMoN/?net=AMoN). These dry deposition data provide more supporting evidence for the wet deposition results, and combined with modeled species not directly measured (e.g. NO_2, N_2O_5 etc.) can be used to produce estimates of total deposition (Schwede and Lear 2014; NADP 2019).

To establish overall multi-site trends, we used random coefficient models (RCMs). When evaluating multiple sites, an RCM is a more powerful statistical tool than a simple regression model because the RCM can account for both within-site and between-site variability. Thus, a trend from a group of sites can be aggregated and assessed simultaneously with more accuracy. This approach has been used in other studies of atmospheric and precipitation chemical species trends. Chan (2009) applied RCMs to assess trends in ground level ozone in Canada and the eastern US, and Butler et al. (2011) used RCMs to investigate relationships between ground-level ozone and NO_x emissions. The RCM approach was also used to assess trends between NO_x emissions and wet and dry atmospheric nitrogen species (Butler et al., 2005), temporal trends in precipitation mercury concentrations in the eastern US (Butler et al., 2008) and temporal trends in ground-level NH_3 concentrations (Butler et al., 2016). More detailed discussions of the use of RCMs can be found in Snijders and Bosker (1999), Raudenbush and Bryk (2002) and Chan (2009).

The trend estimates in this study are obtained using data from all six sites: HB, NY67, DE02, PA15, IL11, TN00 (Fig. 1). The RCMs include a linear and quadratic fixed effect of year, a fixed effect of precipitation amount, and a random intercept and linear slope of year. The SAS mixed model procedure was used (Littell et al., 2006) to fit these models.

3. Results and discussion

3.1. SO_2, NO_x and NH_3 emissions

National emissions of SO_2, NO_x and NH_3 from 1970 to 2017 are shown in Fig. 2. The uptick in NO_x emissions from 2001 to 2002 and the decline in NH_3 emissions from 2000 to 2001 are mainly due to a methodological change in calculating emissions, rather than an actual increase or decrease in emissions (EPA 2019). The marked downward trend in SO_2 and NO_x emissions during 1970–2017 is clear from these long-term data, but the patterns of decline are different. The period from 1970 to 1990 shows a steady decline in SO_2 emissions (largely as a result of the Clean Air Act (CAA) of 1970 and CAA Amendments of 1977). One aspect of the CAA Amendments of 1977 was the establishment of New Source Review (NSR) which promoted installation of up-to-date air pollution control technology on new and renovated industrial facilities to improve air quality in non-attainment regions, and prevent any further air quality degradation in attainment regions (Evans et al., 2008; EPA 2020).

The NO_x values show little or no decline until 1980. From 1980 to the late 1990's NO_x emissions showed a steady decline, but at a lower rate than the decline in SO_2. With the implementation of Phase I of the 1990 CAA Amendments in 1995 for SO_2 and 1996 for NO_x, larger declines for emissions were mandated for SO_2 than for NO_x. However, in efforts to control ozone concentrations from stationary sources, the 1999 Ozone

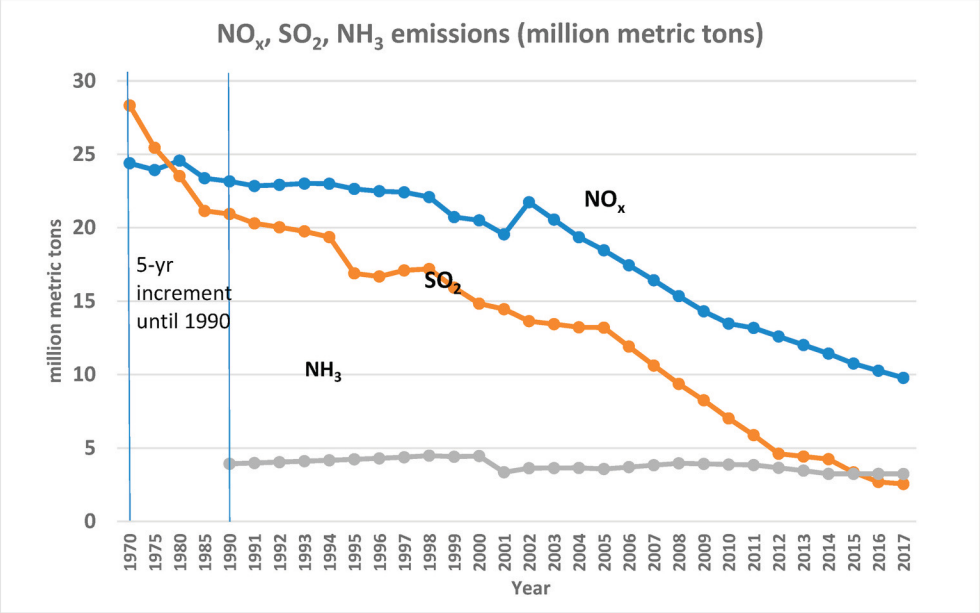

Fig. 2. Annual U.S. emissions of NO_x, SO_2 and NH_3 in million metric tons from 1970 to 2017 (from EPA 2019). The uptick in NO_x emissions from 2001 to 2002 and the decline in NH_3 emissions from 2000 to 2001 are mainly due to a methodological change in calculating emissions.

Transport Commission, and in 2003 the NO_x State Implementation Plan (SIP) allowed for further declines in NO_x (Sickels and Shadwick, 2015; EPA 2017). The Cross State Air Pollution Rule (passed in 2011, but was litigated in the courts until 2014) has also led to further declines in both SO_2 and NO_x emissions in order to help downwind states meet Ambient Air Quality Standards and reduce ozone levels (EPA 2020). Declines in SO_2 and NO_x have also been driven by the closing of coal fired power plants and the replacement of some of these with more cost-competitive and lower emitting natural gas power plants (Pratson et al., 2013). Replacement of coal as a power plant fuel, and a combination of these federal regulations (and some state mandates) has led to a 40% and 34% decline in SO_2 and NO_x, respectively, from 2002 to 2009, and a further 67% and 28% decline, respectively, from 2009 to 2017.

3.2. Hubbard Brook

The 50-calendar-year record of H^+ concentration in bulk precipitation (1964–2014), and the wet-only values (1980–2017) for the HBEF are shown in Fig. 3. Based on these long-term, calendar-year data for annual bulk precipitation, precipitation acidity declined by ~80% during 1964–2014. During the period of overlap (1980–2014), there was a strong convergence between the bulk and wet-only H^+ values (Fig. 3). The long-term decline in SO_4^{2-} in precipitation at Hubbard Brook has been linear and robust (Likens et al., 2001), but some 18 years of continuous monitoring from the beginning of the Study were required to show statistically that acidity of precipitation at Hubbard Brook had been reduced significantly (Likens, 1989).

3.3. The MAP3S/AIRMoN sites

Long-term data on precipitation chemistry from all the AIRMoN sites are available at https://nadp.slh.wisc.edu/AIRMoN/, and previous to 1992 in the Supplemental Material (SM), Part E1, E2 and E3, which includes the MAP3S data record extending back to 1977 as annual volume-weighted values (SM E−1). The more detailed MAP3S event record for all sites is available in SM E−2 and upon request from the NADP Program Office at the Wisconsin State Laboratory of Hygiene, Madison, WI (Larson, pers comm.), and is posted on the NADP website at http://nadp.slh.wisc.edu/dl/map3s/. Environment and Climate Change Canada also has some of the MAP3S data (1977–1982) in http://donnees.ec.gc.ca/data/air/monitor/monitoring-of-atmospheric-precipitation-chemistry/major-ions/LegacyUSANetworks/?lang=en.

The annual precipitation chemistry record for HBEF and the five MAP3S/AIRMoN sites are shown in Fig. 4.

The volume-weighted, annual concentrations for H^+, SO_4^{2-} and NO_3^-, during overlapping periods at all 6 sites are strongly correlated, with r-values of 0.90–0.96, 0.91–0.96 and 0.69–0.91, respectively, and p-values for all the correlations <0.0001. The Ca^{2+} and NH_4^+ correlations between sites are much weaker, with only 4 of 30 and 6 of 30 correlations, respectively, having p-values ≤ 0.01. The multivariate correlations (r-values and p-values of correlations) for H^+, SO_4^{2-}, and NO_3^-, Ca^{2+} and NH_4^+ are included in the Supplementary Material, Part F.

Fig. 4 does not include the years 1990 and 1991 for the MAP3S/AIRMoN sites, because this was a transition period from MAP3S to NADP/AIRMoN and the yearly records for 1990 and 1991 are incomplete. The Ca^{2+} concentrations at NY67 and PA15 for 1977 are not included because there are no data for January to August (see Supplementary Material, Part E−1 and E−2). Calcium values for the Ithaca and Aurora sites for 1970-71 were not included in the trend analysis because they appeared as possible outliers, probably because of the bulk sampling. The trend analysis was done both by including and by omitting Ca^{2+} data for 1970-71; the results were not significantly different (% change of −14%, in both cases, is the same from 1981 to 2017). Using random coefficient mixed models, we calculated the overall changes in concentrations for Hubbard Brook and the five long-term MAP3S/AIRMoN sites (NY67, PA15, DE02, IL11 and TN00) combined. For the period 1981 to 2017, there were substantial declines of 85% for H^+, 80% for SO_4^{2-} and 66% for NO_3^-; Ca^{2+} showed a 14% decline and NH_4^+ had a <1% decline (Table 4). The longer record at Hubbard Brook (Fig. 4 a) shows a sharp decline in Ca^{2+} (and Mg^{2+}, Likens, 2013) concentration between 1965 and ~1980; concentrations are relatively flat thereafter in accordance with the results from the other long-term MAP3S/AIRMoN sites (Fig. 4 b-f). The data are also presented by each ionic species (e.g. H^+, SO_4^{2-}, NO_3^-, $NH_4^+$and Ca^{2+}) as opposed to by site as shown in Fig. 4, in Supplementary Material, Part G. In addition to the annual data, Part G includes the non-linear (quadratic) regression lines for the overall six site trends, and the individual site trends.

The decline in Ca^{2+} concentrations at Hubbard Brook between 1963

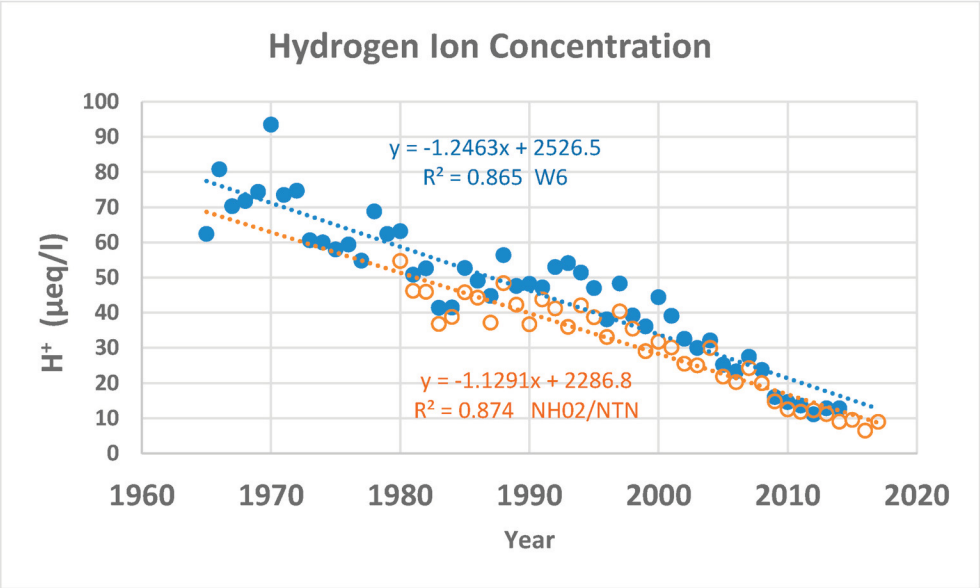

Fig. 3. A 50-year record of acid precipitation, measured in H^+ concentration (µeq/l), at Hubbard Brook Experimental Forest, based on weekly bulk precipitation chemistry from Watershed 6. Each solid dot is the annual, volume-weighted, calendar year concentration. These data, including the linear regression, are compared with the annual wet-only NADP/NTN values (NH02) at Hubbard Brook from 1980 to 2017 (open circles).

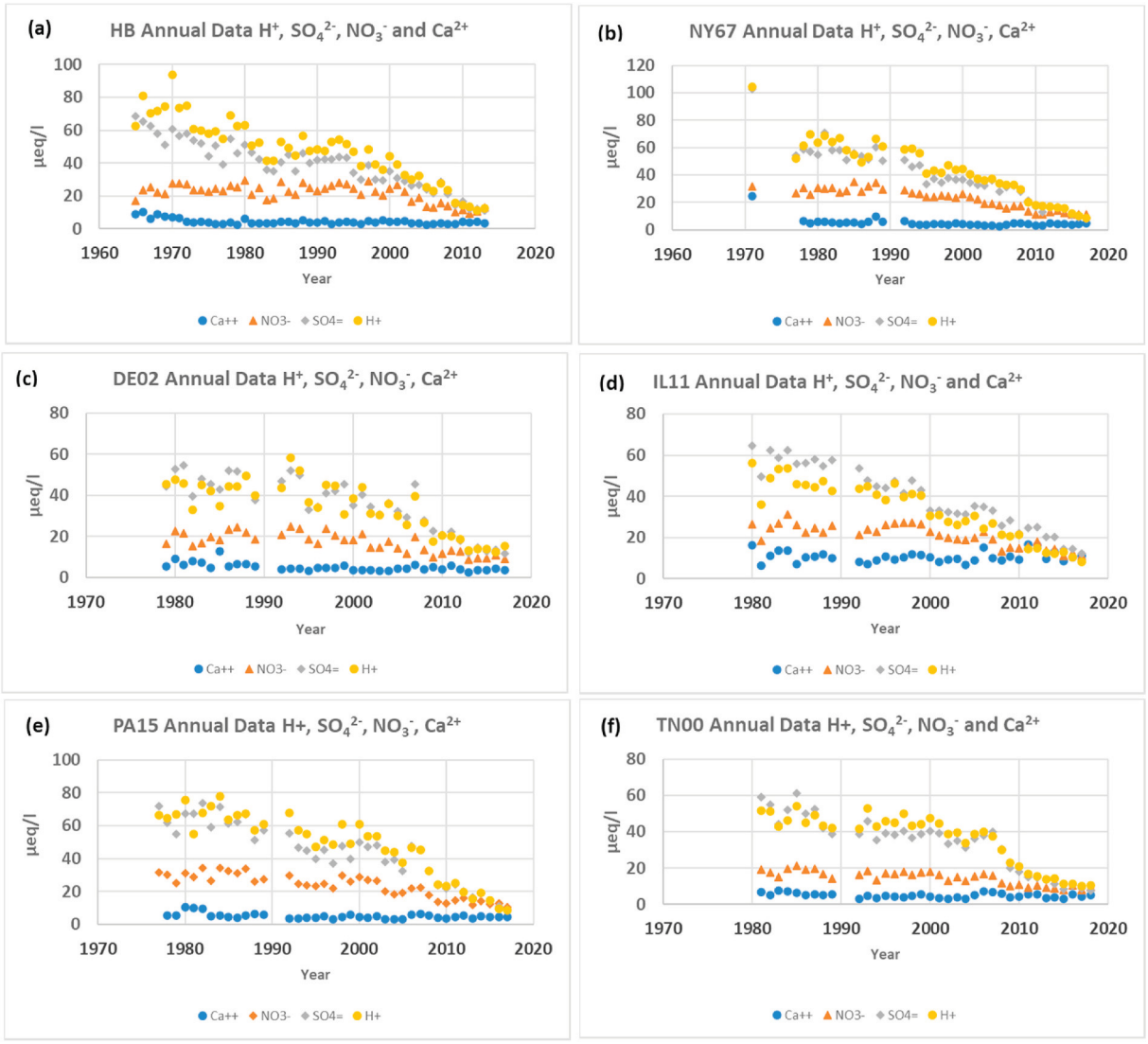

Fig. 4. Annual, volume-weighted, mean concentrations of H^+, SO_4^{2-}, NO_3^- and Ca^{2+} for Hubbard Brook (HB), and the 5 long-term MAP3S/AIRMoN sites (NY67, DE02, PA15, IL11 and TN00). NY67 includes the average 1970–1971 data for the Ithaca Game Farm (GF) and Aurora Research Farm sites located near NY67 (see section 3.2 for further details).

and ~1980 are associated with decreases in national emissions of particulate matter from major sources that occurred during this period (Table 3; and EPA 1976, 1977, 1978, 1991). The IL11 station has consistently higher concentrations of Ca^{2+} than the other stations, possibly because of washout from calcium-containing dust from nearby agricultural areas.

The NO_3^- concentrations in precipitation peaked in the mid-1980s and current values are quite low, about 25% of what they were in the mid-1980s (Fig. 4). A steep decline in SO_4^{2-} concentrations has occurred at all sites (~80%; Fig. 4 and Table 4).

Emissions of SO_2 and NO_x peaked in late-1960s – early-1970s (Fig. 2). Correlated with these high levels of emissions, acidification in precipitation peaked in the late-1960s-early- 1970s in the northeastern U.S. and then declined thereafter (Likens, 2013; Likens and Buso 2012; Holmes and Likens 2016). Present national precipitation chemistry networks were established after this peak, but fortunately, the Hubbard Brook record started in 1963 and captured this early trend (Fig. 3).

Table 3
Estimates of particulate matter emissions for the United States by source category (mton x 10^6/yr; data from EPA 1976, 1977, 1978 and 1991).

Source	1970	1987	% Change
Industrial Processes	10.5	2.5	−76
Fuel Combustion	4.6	1.8	−61
Solid Waste Incineration	1.1	0.3	−73
Miscellaneous[a]	1.1	1.0	−9
Transportation	1.2	1.4	+17
TOTAL	18.5	7.0	−62

[a] e.g. forest fires.

Table 4
Changes in annual precipitation concentrations from 1981 to 2017 for combined sites of Hubbard Brook and the five long-term MAP3S/AIRMoN sites. Values in parentheses are the standard errors of the estimated annual average, volume-weighted means.

Ion	Date - 1981	Date - 2017	% change
H^+	57.41 (4.07) µeq/l	8.72 (2.23) µeq/l	−85%
SO_4^{2-}	2.72 (0.11) mg/l	0.53 (0.07) mg/l	−80%
NO_3^-	1.51 (0.13) mg/l	0.51 (0.03) mg/l	−66%
Ca^{2+}	0.14 (0.02) mg/l	0.12 (0.02) mg/l	−14%
NH_4^+	0.268 (0.021) mg/l	0.267 (0.039) mg/l	<1%

3.4. Long-term changes in precipitation amount

Annual precipitation amount changed relatively little at the long-term MAP3S/AIRMoN sites during 1981–2017 (see Supplemental Material, Part C). However, annual precipitation at Hubbard Brook increased from ~1350 mm in 1895 to ~1600 mm in 2010 (Likens, 2013), increasing since the mid-1950s at a rate of ~5.3 cm/decade, more during summer than winter (Holmes and Likens, 2016). Annual variability in precipitation amount was much greater after about 1960. The long-term trend at Hubbard Brook is possibly a signal of climate change (Holmes and Likens 2016).

The temporal decrease in flux of chemicals in precipitation at the MAP3S/AIRMoN sites is therefore mainly dependent on change in concentration rather than a change in precipitation amount. Wet deposition changes are thus proportionally quite similar to the changes in concentrations (see Table 4 and Supplemental Material, Part B – Table S1).

3.5. Dry deposition

The decline in dry deposition of NO_3^- and S (Supplemental Material, Part D and Fig. 5) parallel that for emissions of SO_2 and NO_x (Fig. 2) and wet deposition (Fig. 4). Declines from 2000 to 2017 for dry deposition of $SO_2 + SO_4^{2-}$(p), and NO_3^-(p) plus HNO_3^-, are 87% and 64%, respectively for the combined sites of HB, NY67, PA15, IL11 and TN00 (Table 5). The Hubbard Brook values for dry deposition are lower than the other sites (SM, Part D, Figures S 6–9), probably reflecting the more rural, more forested, less agricultural nature of the Hubbard Brook site (Holmes and Likens 2016).

The significant declines in H^+, SO_4^{2-} and NO_3^- concentrations, and related dry deposition species, are directly correlated with the declines in emissions of SO_2 and NO_x mainly due to clean air legislation, especially the Amendments of 1970 and 1990 (Fig. 2), (e.g. Butler et al., 2001; 2005; 2011; Likens et al., 2005; Feng et al., 2019). The six-site range in r-values for combined annual U.S. emissions of SO_2 plus NO_x vs annual wet H^+ concentrations, SO_2 emissions vs wet SO_4^{2-} concentrations, and NO_x emissions vs wet NO_3^- are 0.89–0.96, 0.92 to 0.95, and 0.81 to 0.90, respectively. The five-site (there are no dry data for DE02) range in r-values for SO_2 emissions vs dry S and NO_x emissions vs dry NO_3^- are 0.92–0.97 and 0.92 to 0.97, respectively. The p-values for all of these relationships are <0.0001. See Supplemental Material, Part H, for individual correlations.

In contrast, ammonia (NH_3) emissions are unregulated and show little change in emissions (Fig. 2) and an increase in air concentrations since 2007 over large areas of the U.S. (Butler et al., 2016; Warner et al., 2017). Declining SO_2 and NO_x emissions have led to reduced atmospheric acidity, offering less potential for reduced NH_3 concentrations from scavenging by acidic species (e.g. H_2SO_4 and HNO_3). Warner et al. (2017) also includes higher soil temperatures as another factor increasing the rate of NH_3 emissions, and thus leading to higher NH_3 air concentrations. Ammonium concentrations in precipitation at these sites have changed very little during this 40-year period (Table 4).

3.6. Acid rain

A prominent theme of these long-term data on precipitation chemistry describes the discovery of acid rain (1963), peaking of acidity in the early 1970s, and then declining acidity to the present time. Sulfuric acid is the dominant acid in precipitation, but nitric acid has been increasing proportionally during recent years (Likens, 2013). The overall pattern of acidification and recovery in stream water at the HBEF follows the form of an hysteresis for the annual balance between acid anions (SO_4^{2-} plus NO_3^-) and sum of base cations (Ca^{2+}, Mg^{2+}, Na^+, K^+). The current downward trajectory in precipitation concentrations of SO_4^{2-} and NO_3^- is toward acidic values that could be even lower than pre-industrial revolution values (Likens and Buso 2012; Likens, 2013; Holmes and Likens 2016). As such, this pattern represents a major environmental success story where the U.S. CAA of 1963 and1970 and the CAA Amendments of 1977 and 1990 curbed acid-forming emissions from the combustion of fossil fuels; the acidity of precipitation decreased markedly in concert (e.g. Figs. 2–4; e.g., Likens 2010, Likens, 2013; Holmes and Likens 2016). The 1970 CAA required comprehensive federal and state regulations for both stationary and mobile sources of air pollution, which resulted in reduction of emissions of sulfur-containing particles from smokestack scrubbing and controls on vehicular emissions. The 1990 Amendments were the first federal legislation in the U.S. to address directly and explicitly the problems of acid rain by reducing emissions of SO_2 and NO_x, starting in the mid-1990s. The 1990 Amendments required a reduction of 10 million tons (9.1 million metric tons) of SO_2 emissions per year and reductions of 1.2 million tons (1.1 million metric tons) of NO_x emissions per year below 1980 levels by the year 2000 (Likens,

Table 5
Changes in dry deposition of sulfur ($SO_2 + SO_{4\,(p)}^{2-}$), dry NO_3^- ($HNO_3^- + NO_{3\,(p)}^-$) and dry Ca^{2+} from 2000 to 2017 based on the data from the combined sites of Hubbard Brook (NH02/WST109 = NADP/CASTNET) and the 4 co-located, long-term MAP3S/AIRMoN sites (NY67/CTH 110, PA15/PSU 106, IL11/BVL 130 and TN00/ONL 102). Values in parentheses for dry NO_3^- are the standard errors of the predicted annual values. The data for dry S and Ca^{2+} were log transformed to meet the assumptions of the model (e.g. normality and constant variance of the residuals). Back-transformed values and their 95% confidence intervals in parentheses are presented in the Table.

Ion	Date - 2000	Date - 2017	% change
Dry S	**8.05** (2.99–21.65) kg S/ha	**1.06** (0.53–2.11) kg S/ha	**−87%**
Dry NO_3^-	**3.93** (0.63) kg N/ha	**1.41** (0.18) kg N/ha	**−64%**
Ca^{2+}	**1.21** (0.82–1.80) kg Ca/ha	**1.21** (0.73–2.02) kg Ca/ha	**<1%**

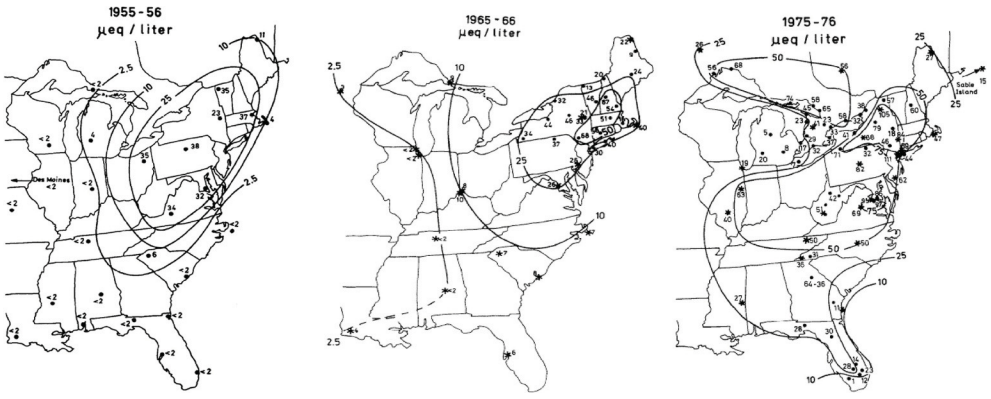

Fig. 5. Early maps of changes in precipitation acidity, as μeq H^+/l, from the mid-1950's to the mid-1970's, before the establishment of NADP (modified from Likens and Butler, 1981).

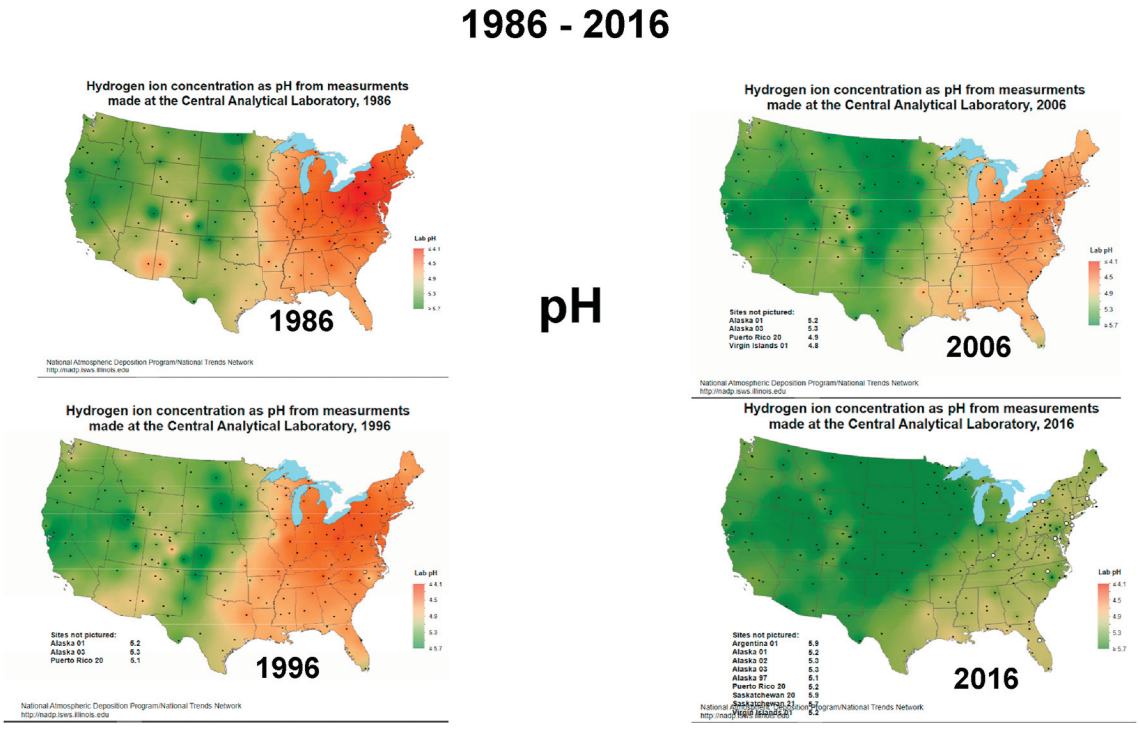

Fig. 6. NADP maps showing the annual volume-weighted pH changes in precipitation chemistry from 1986 through 2016. Dots on the maps indicate locations of NADP sites used to draw the maps. Source: https://nadp.slh.wisc.edu/NTN/maps.aspx.

2013).

Concentrations of H^+, SO_4^{2-}, and NO_3^- in precipitation are trending toward ~10 ueq/L at all sites shown in Fig. 4. Because of the large declines in concentration of the major ions in precipitation, the overall solute strength in precipitation has become surprisingly dilute, especially at the Hubbard Brook site (Likens and Buso 2012).

Early attempts to map the extent and intensity of acid precipitation in eastern North America, even though available data were meager, clearly showed the spread and intensification of acid rain in the northeastern U.S. from the mid 1950's to the mid 1970's (Fig. 5). The visualization provided by these early maps (Cogbill and Likens 1974; Likens and Butler 1981) was important in bringing this complex environmental problem to the attention of the public and to decision makers. The role of cartoons was also probably important. The satire of cartoons has been used effectively in numerous political/policy issues to influence public opinion (see, www.un.org/apps/news/story.asp?NewsID=20274&Cr=cartoon&Cr1). It is our opinion that they served the same purpose in the acid rain debates (see Holmes and Likens 2016).

These early maps were limited in data, but the generalized iso-lines of acidity that could be drawn provided an understandable picture of the extent and intensity of precipitation chemistry, and more importantly the temporal changes that were occurring in eastern North America. The early maps for acidity during 1955–1956 and 1965–1966 were based on predicted pH values (Cogbill and Likens 1974). The map for 1975-76 was based on measured pH values by many individuals. We had

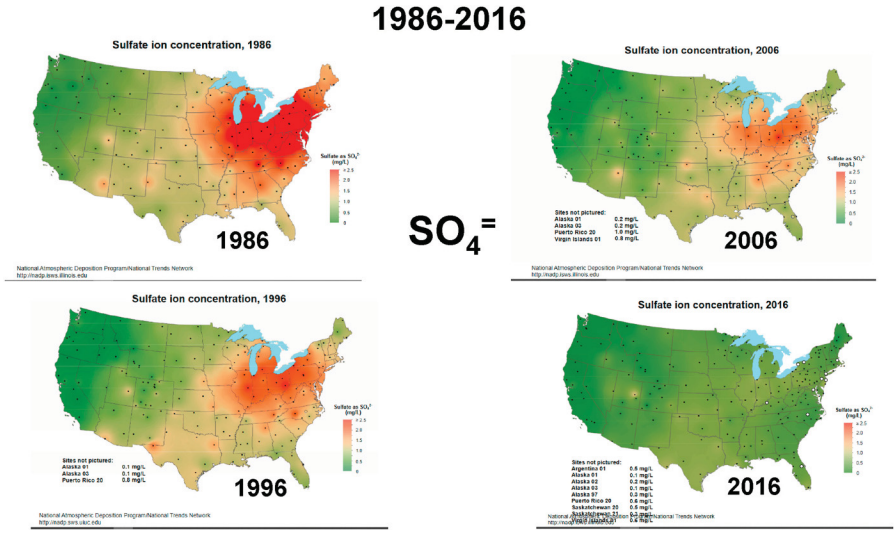

Fig. 7. NADP maps showing the annual volume-weighted SO_4^{2-} concentration changes in precipitation chemistry from 1986 through 2016. Dots on the maps indicate locations of NADP sites used to draw the maps. Source: https://nadp.slh.wisc.edu/NTN/maps.aspx.

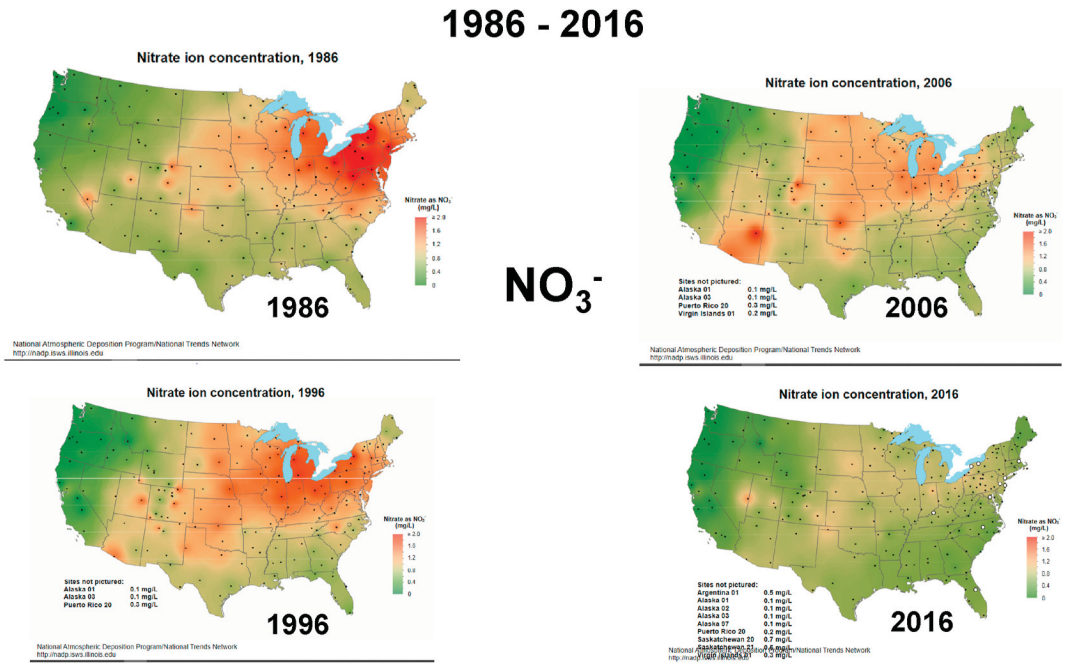

Fig. 8. NADP maps showing the annual volume-weighted NO_3^- concentration changes in precipitation chemistry from 1986 through 2016. Dots on the maps indicate locations of NADP sites used to draw the maps. Source: https://nadp.slh.wisc.edu/NTN/maps.aspx.

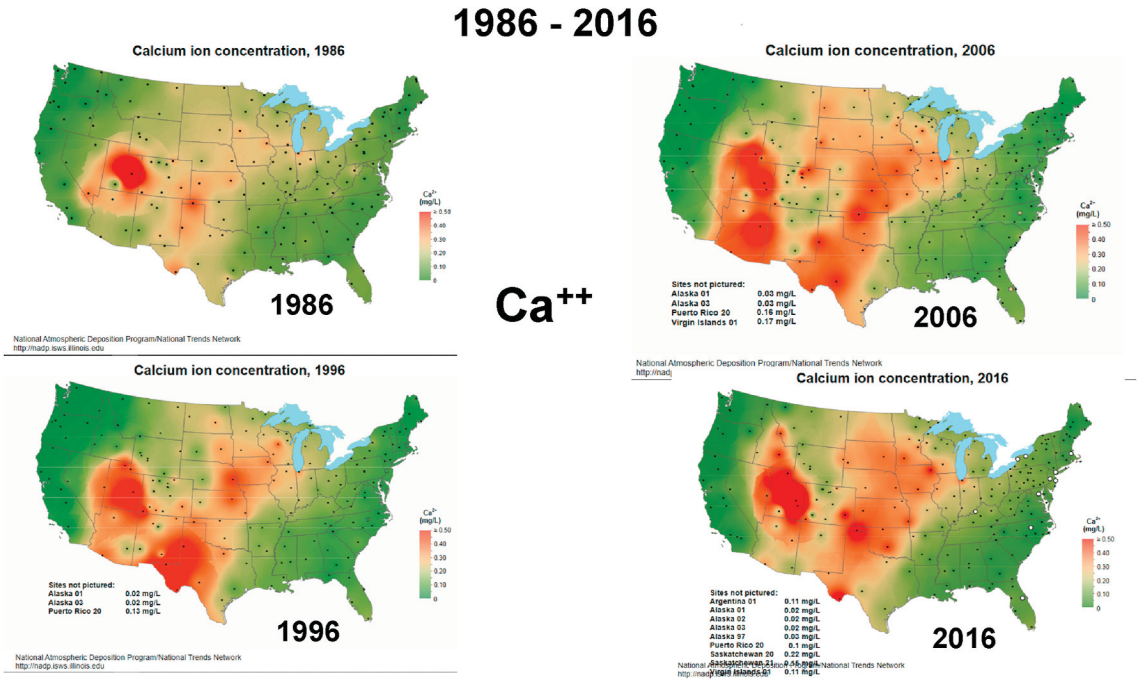

Fig. 9. NADP maps showing the annual volume-weighted Ca^{2+} concentration changes in precipitation chemistry from 1986 through 2016. Dots on the maps indicate locations of NADP sites used to draw the maps. Source: https://nadp.slh.wisc.edu/NTN/maps.aspx.

contacted everyone we knew in eastern North America that was measuring precipitation chemistry and asked them to share their data so that we could construct the 1975-76 map (Likens and Butler 1981). There were limited regional networks, but no national networks in existence measuring precipitation chemistry prior to 1976. These early maps were based on data from Junge and Werby (1958), Lodge et al. (1968), Gambell and Fisher (1966), Pearson and Fisher (1971), Likens et al. (1972), and Likens and Butler (1981). We recognize combining data from different sources for a "secondary use" (e.g. establishing long-term patterns in precipitation chemistry), which has been used in this study, has challenges associated with it (e.g. different methodologies and methods of reporting the data). However, "secondary use" of data is common and is a valuable and cost-effective approach (Sprague et al., 2017).

Current maps developed from data generated by the widespread NADP precipitation chemistry network now in place across the United States are much more data-rich and accurate (Figs. 6, 7, 8 and 9). As such, they are clearly not only informative, but also compelling in describing the status and temporal change in precipitation chemistry throughout the northeastern U.S., and elsewhere. Arguably, these maps

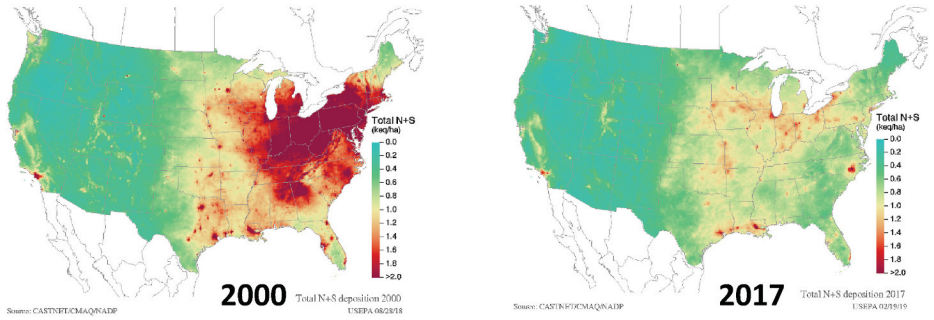

Fig. 10. Total (wet + dry) sulfur and nitrogen, (in keq/ha) combined deposition for the years 2000 and 2017 (From NADP, 2019). Source: https://nadp.slh.wisc.edu/committees/tdep/tdepmaps/.

are among the most important products of the national precipitation chemistry networks.

3.7. Total atmospheric deposition

In recent years NADP in collaboration with CASTNET has developed total deposition (wet + dry) maps. Deposition of unmeasured species, such as HONO, N_2O_5, PAN, and organic nitrate are included from model results (Schwede and Lear 2014) and provide an opportunity to estimate total atmospheric deposition on a national scale (e.g. Fig. 10). Nation-wide maps clearly reinforce the trend of drastic regional atmospheric reductions in sulfur and nitrogen components since 2000 and before (see Fig. 10 and Likens and Butler 2017). Given current, proposed federal policy changes regarding controls on national emissions, these maps, showing temporal change, will be critically important in the future to document any further changes that might occur to precipitation chemistry.

3.8. Some concluding thoughts

The National Atmospheric Deposition Program (NADP) now has had over 40 years of successful operations. There are several key features underpinning the success of such a large and complicated network, including the talented and dedicated operators of the individual sites, and that all chemical analyses were done at one Central Analytical Laboratory. The Network has provided critically important, long-term data characterizing the status, changes, and temporal trends for precipitation chemistry throughout the U.S., i.e. high-quality, spatial and temporal data for a large area. This network has the characteristics of a successful, long-term monitoring program (Table 2). Nevertheless, some might say, "Isn't 40 years enough?" Arguably, however, it has never been more important to continue this network without interruption to monitor changes in precipitation chemistry, given the potential impact on air chemistry of both real changes that are occurring and will occur, and changes from proposed new rules governing clean air regulations, on emissions, on receiving ecosystems and on federal policy (see, Table 1). Moreover, the Network now has value far beyond its original aspirations and goals. For example, network data have become valuable to climate research, e.g. in verifying climate models (Yahya et al., 2017), and documenting climatic changes (Wetherbee and Mast (2016).

Hubbard Brook and NADP have played major roles in helping to protect the chemistry of the atmosphere in the U.S. If NADP were to be dismantled for some unforseen reason, it would be very difficult, if not impossible, to restore the program to its current effective state. To recreate the complicated nature of site administration, skilled operation and coverage, the diversity of funding, including in-kind support, and operator dedication that have developed over the decades, and the professional leadership of a central analytical laboratory, would be extremely difficult and expensive. This is the kind of hypothesis that should not be tested.

4. Summary

Continuous, long-term monitoring of precipitation chemistry began at the Hubbard Brook Experimental Forest in 1963, and was followed by various large-scale monitoring networks (the MAP3S network (1976), the NADP/NTN network (1978), the NADP/AIRMoN network (1992), and the dry deposition, NDDN/CASTNET (1987) network). The temporal and spatial changes in precipitation chemistry for the northeastern U.S. from 1963 to the present are best shown by combining records from all of these stations and networks. The discovery of acid rain in North America occurred at Hubbard Brook in 1963. Indicators of changing atmospheric chemistry were critical for initiating federal policy necessary for improving air quality and for reducing atmospheric pollutant loading, which had led to acid rain in this area, starting in the 1950s. Marked declines in national emissions of SO_2 and NO_x, major precursors of acid rain, have occurred since 1970 and are driven by federal legislation. Analyzing combined records from Hubbard Brook and the 5 longest operating MAP3S/AIRMoN sites (IL11, NY67, DE02, PA15 and TN00) with a random coefficient, mixed-model showed overall declines in annual concentrations of H^+, SO_4^{2-} and NO_3^- from 1981 to 2017 of 85%, 80% and 66%, respectively. Calcium concentration declined by 14% and NH_4^+ showed no change during this period. Dry deposition of sulfur, NO_3^- and Ca^{2+} measured at co-located NDDN/CASTNET sites showed declines of 87%, 64% and <1%, respectively, during 2000–2017, paralleling declines in atmospheric emissions and wet deposition. Long-term records of precipitation amount at Hubbard Brook show wetter conditions since about 1900, whereas no trends are shown in the shorter records of precipitation amount from the 5 longest operating MAP3S/AIRMoN sites.

CRediT authorship contribution statement

Gene E. Likens: Writing - original draft, was responsible for, Conceptualization, and organization and writing of the paper. **Thomas J. Butler:** Writing - original draft, was responsible for organization and writing of the paper. **Rodger Claybrooke:** Data curation, were responsible for obtaining and aggregating the NADP, MAP3S and NADP data. **Francoise Vermeylen:** Formal analysis, was responsible for much of the statistical analysis especially running the RCM models. **Robert Larson:** Data curation, were responsible for obtaining and aggregating the NADP, MAP3S and NADP data, also produced some of the figures.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

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