

# Trends in cation, nitrogen, sulfate and hydrogen ion concentrations in precipitation in the United States and Europe from 1978 to 2010: a new look at an old problem

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**Abstract** Industrial emissions of  $\text{SO}_2$  and  $\text{NO}_x$ , resulting in the formation and deposition of sulfuric and nitric acids, affect the health of both terrestrial and aquatic ecosystems. Since the mid-late 20th century, legislation to control acid rain precursors in both Europe and the US has led to significant declines in both  $\text{SO}_4\text{-S}$  and  $\text{H}^+$  in precipitation and streams. However, several authors noted that declines in streamwater  $\text{SO}_4\text{-S}$  did not result in stoichiometric reductions in stream  $\text{H}^+$ , and suggested that observed reductions in base cation inputs in precipitation could lessen the effect of air pollution control on improving stream pH. We examined long-term precipitation chemistry (1978–2010) from nearly 30 sites in the US and Europe that are variably affected by acid deposition and that have a variety of industrial and land-use histories to (1) quantify trends in  $\text{SO}_4\text{-S}$ ,  $\text{H}^+$ ,  $\text{NH}_4\text{-N}$ , Ca, and  $\text{NO}_3\text{-N}$ , (2) assess stoichiometry between  $\text{H}^+$  and  $\text{SO}_4\text{-S}$  before and after 1990, and (3) examine regional synchrony of trends. We expected

that although the overall efforts of developed countries to reduce air pollution and acid rain by the mid-late 20th century would tend to synchronize precipitation chemistry among regions, geographically varied patterns of fossil fuel use and pollution control measures would produce important asynchronies among European countries and the United States. We also expected that control of particulate versus gaseous emission, along with trends in  $\text{NH}_3$  emissions, would be the two most significant factors affecting the stoichiometry between  $\text{SO}_4\text{-S}$  and  $\text{H}^+$ . Relationships among  $\text{H}^+$ ,  $\text{SO}_4\text{-S}$ ,  $\text{NH}_4\text{-N}$ , and cations differed markedly between the US and Europe. Controlling for  $\text{SO}_4\text{-S}$  levels,  $\text{H}^+$  in precipitation was significantly lower in Europe than in the US, because (1) alkaline dust loading from the Sahara/Sahel was greater in Europe than the US, and (2) emission of  $\text{NH}_3$ , which neutralizes acidity upon conversion to  $\text{NH}_4^+$ , is generally significantly higher in Europe than in the US. Trends in  $\text{SO}_4\text{-S}$  and  $\text{H}^+$  in precipitation were close to stoichiometric in the US throughout the period of record, but not in Europe, especially eastern Europe. Ca in precipitation declined significantly before, but not after 1990 in most of the US, but Ca declined in eastern Europe even after 1990.  $\text{SO}_4\text{-S}$  in precipitation was only weakly related to fossil fuel consumption. The stoichiometry of  $\text{SO}_4\text{-S}$  and  $\text{H}^+$  may be explained in part by emission controls, which varied over time and among regions. Control of particulate emissions reduces alkaline particles that neutralize acid precursors as well as S-containing

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particulates, reducing  $\text{SO}_4\text{-S}$  and Ca more steeply than  $\text{H}^+$ , consistent with trends in the northeastern US and Europe before 1990. In contrast, control of gaseous  $\text{SO}_2$  emissions results in a stoichiometric relationship between  $\text{SO}_4\text{-S}$  and  $\text{H}^+$ , consistent with trends in the US and many western European countries, especially after 1991. However, in many European countries, declining  $\text{NH}_3$  emissions contributed to the lack of stoichiometry between  $\text{SO}_4\text{-S}$  and  $\text{H}^+$ . Recent reductions in  $\text{NO}_x$  emissions have also contributed to declines in  $\text{H}^+$  in precipitation. Future changes in precipitation acidity are likely to depend on multiple factors including trends in  $\text{NO}_x$  and  $\text{NH}_3$  emission controls, naturally occurring dust, and fossil fuel use, with significant implications for the health of both terrestrial and aquatic ecosystems.

**Keywords** Acid deposition · Ammonium · Base cations · Clean air act · EMEP · LTER · NADP · Nitrate · Sulfate

## Introduction

Human activity, whether from industry or urbanization, or management activities such as road construction, forestry, or grazing, can profoundly affect precipitation chemistry and nutrient delivery to natural ecosystems. Of particular interest in urban regions and regions downwind of industrial activity and power plants is the emission of  $\text{SO}_2$  and  $\text{NO}_x$  resulting in the formation and deposition of sulfuric and nitric acids. Acid rain has had significant effects on both terrestrial and aquatic ecosystems (Aber 1982; Stoddard et al. 1999; Norton and Vesely 2003; Oulehle et al. 2008; Burton and Aherne 2012; Pannatier et al. 2005), and there is significant concern over both the mechanisms and the pace of recovery from historically high acidic precursor loads (Baker et al. 1991; Rusek 1993; Schindler 1988; Schulze 1989; Sullivan et al. 1990; Warby et al. 2009). Countries have, at different times, employed different measures to reduce  $\text{SO}_2$  emissions (including using low S coal, washing coal, using scrubbers and other filter control technology, and switching to natural gas or other energy sources). In the US, the Clean Air Act was passed in 1963 with significant amendments in 1970 and 1990 that regulated and reduced emissions, and concentrations of sulfate in receiving waters of the eastern United States declined

(Driscoll et al. 1989; Likens et al. 1996). In Europe, the Convention on Long-range Transboundary Air Pollution was signed in 1979, entered into force in 1983, and has been extended by eight specific protocols that have progressively reduced emissions.

In response to emissions controls and changes in economic activity,  $\text{SO}_2$  emissions have declined since 1970 in North America and Europe and somewhat later in eastern Europe and the former Soviet Union (Smith et al. 2011). However, in New England the long-term decline in streamwater sulfate concentrations did not result in the expected stoichiometric increase in stream pH (Driscoll et al. 1989). Instead, both sulfate and base cations declined in precipitation at Hubbard Brook (Likens et al. 1984). To examine the generality of the patterns of declining cations in precipitation seen in the long-term analysis of Hubbard Brook data, Hedin et al. (1994) expanded the analysis to include a number of sites in the US with long-term precipitation chemistry data as well as two long-term monitoring stations in Europe. They found that linear trends for the sum of base cation concentrations in precipitation were negative from 1979 to 1990 at all east coast US NADP sites examined. Similar declines in non-sea salt base cation deposition were observed in Sweden and the Netherlands. They suggested that the declines in base cation deposition were synchronous and might have common causes, and might cancel out expected declines in precipitation acidity from declines in sulfate.

However, relationships among  $\text{SO}_2$  emissions,  $\text{SO}_4\text{-S}$  in precipitation, cation deposition, and precipitation pH are complex, so changes in base cations may have varied effects on precipitation pH. Base cations per se cannot neutralize acid precipitation, but carbonates, hydroxides, and ammonia ( $\text{NH}_3$ ) can. If the only or dominant substance entering the atmosphere were  $\text{SO}_2$ , then the relationship between  $\text{SO}_4\text{-S}$  and  $\text{H}^+$  would be stoichiometric, and reducing  $\text{SO}_2$  would have the effect of increasing rainfall pH. However, emissions from industry and from fossil fuel-supplied power plants contain more than just gases. Fly ash (ash that does not settle out after coal burning in power plants) may contain sulfates and lime ( $\text{CaO}$ ). Fly ash is basic, because lime is quickly converted to  $\text{Ca}(\text{OH})_2$  in the presence of water; hence, emissions controls on fly ash may reduce both cation and sulfate concentrations in precipitation with the paradoxical effect of increasing rainfall  $\text{H}^+$ . If fly ash

contains predominantly salts, emissions controls will reduce  $\text{SO}_4\text{-S}$  and cations with negligible effects on rainfall  $\text{H}^+$ . Only controls on  $\text{SO}_2$  emissions should have positive and stoichiometric effects on rainfall  $\text{H}^+$ .

Moreover, cations from both natural and anthropogenic sources contribute to atmospheric deposition. Sea spray dominates natural inputs of Na and Mg, especially in ecosystems near the ocean. Dust derived from Africa, Asia, and Australia is a significant natural source of cations, especially Ca, although estimates of total deposition inputs are highly variable (Grini et al. 2005). Although dust transport and deposition has generally been ascribed to drought, human activities such as agriculture, grazing, road construction, or logging have been shown to affect dust transport in Africa (Martinez-Garcia et al. 2011; Mulitza et al. 2010) and in the US (Neff et al. 2008). Dust from Africa can dominate atmospheric deposition of cations to terrestrial ecosystems throughout much of Europe, especially southern Europe (Draaijers et al. 1997). The dominant anthropogenic sources of cations in precipitation are the combustion of fossil fuels, specifically coal and wood fuels, and industrial processes such as cement or steel production. Emissions of  $\text{SO}_2$ , fly ash, and salts depend on the fuel used (coal contains significantly more contaminants than liquid fossil fuels) and the control systems in place in individual plants.

$\text{NH}_3$  is highly reactive in the atmosphere and can neutralize atmospheric acids by forming  $\text{NH}_4\text{-}$ containing aerosol salts, consuming a proton in the process, and can deposit rapidly to surfaces, including vegetation.  $\text{NH}_3$  aerosols contribute to the loading of excess N to receiving ecosystems and the aerosols themselves are considered to be detrimental to human health. In both Europe and the United States, the largest sources of  $\text{NH}_3$  emissions are agricultural, primarily from livestock waste and fertilizer (Battye et al. 1994), with smaller contributions from catalytic converters and vehicles (Fraser and Cass 1998). There may be additional emissions from undisturbed soils and biomass burning as well (Metcalf et al. 1989; Schlesinger and Hartley 1992; Clarisse et al. 2009). Changes in  $\text{NH}_3$  emissions could be a significant source of a lack of stoichiometry between  $\text{SO}_4\text{-S}$  and  $\text{H}^+$ , but this has not been quantified. Particularly in Europe, ceilings on emissions and management practices have been in place to reduce  $\text{NH}_3$  loading to the

atmosphere, but these vary regionally. The spatial and temporal scale of  $\text{NH}_4\text{-N}$  deposition is complicated by interactions between  $\text{SO}_2$ ,  $\text{NO}_3$  and  $\text{NH}_3$ .  $\text{NH}_3$  preferentially forms one of several ammonium sulfate salts as an aerosol, which can be transported over longer distances than the reactive  $\text{NH}_3$  phase, thus increasing the transport of both  $\text{NH}_4\text{-}$  and  $\text{SO}_4\text{-S}$ . Excess  $\text{NH}_3$  can react with  $\text{NO}_3$ , in the atmosphere, forming the  $\text{NH}_4\text{NO}_3$  aerosol, which, although relatively labile, can increase the transport distance of both  $\text{NH}_4\text{-}$  and  $\text{NO}_3\text{-N}$ . If  $\text{NH}_3$  levels exceed  $\text{NO}_x$  and  $\text{SO}_2$  emissions, the reactive  $\text{NH}_3$  is deposited more locally (Lehmann et al. 2007). Thus transport of  $\text{NH}_3$  is partly determined by atmospheric concentrations of  $\text{SO}_2$  and  $\text{NO}_3$ , and declining  $\text{SO}_2$ , for example, could cause more local deposition of reactive  $\text{NH}_3$ .

Trends in emissions of  $\text{SO}_2$  and cations, as well as  $\text{NH}_4\text{-}$  and  $\text{NO}_3$ , vary regionally and change over time. Emissions of  $\text{SO}_2$  in 1970 were, on average, almost twice as high in Europe as in the US on an areal basis (Erisman and Draaijers 1995). Responding gradually to emission controls, emissions in the US and western Europe peaked in the early 1970s and have declined steadily since then, but emissions did not decline until 1980 or later in eastern Europe (Smith et al. 2011). Patterns of natural dust inputs also differ significantly between Europe and the US. In the US, early controls on particulate emissions from power plants and industry (1970s–1990) would be expected to have reduced both cations and sulfates in precipitation, with complex effects expected on rainfall pH, whereas emissions controls since 1990 may have regulated  $\text{SO}_2$  directly, with stoichiometric effects on rainfall pH.

To capture these varying and lagged influences on precipitation acidity, this study examined 30-year trends in precipitation chemistry from  $\sim 30$  sites in the US and Europe that are variably affected by acid deposition and that have a variety of industrial and land-use histories. We tested whether (1) previously reported declines in cation deposition were synchronous in the US and Europe, and persistent since 1990; (2) temporal patterns in changes in  $\text{SO}_4\text{-S}$  and  $\text{H}^+$  were synchronous with changes in cation deposition; and (3) non-stoichiometric differences in  $\text{SO}_4\text{-S}$  and  $\text{H}^+$  could be explained by trends in cation,  $\text{NH}_4\text{-N}$ , or  $\text{NO}_3\text{-N}$  deposition. We also explored relationships between fossil energy use and patterns of  $\text{H}^+$ ,  $\text{SO}_4\text{-S}$ , and cations in deposition. We hypothesized that declining cations in deposition, while common, would

not be universal or synchronous across the US and throughout Europe, but would be more related to regional patterns of energy consumption and pollution control measures, as well as to differences in natural background deposition patterns.

### Study sites

Study sites were selected from European and US records of long-term precipitation chemistry, focusing on sites in locations, such as forests, that were distant from obvious point sources of air pollutants (i.e., urban, industrial areas) or sources of dust from anthropogenic activities (i.e., agriculture). All publically available long-term precipitation chemistry records from the US and European sources were inspected, and sites were selected that provided broad coverage of the Europe and the US and had continuous records extending from the mid-1970s or mid-1980s to present (Fig. 1).

### Data sources

The study was conducted using publically available data from the National Atmospheric Deposition Program (NADP) for the United States (<http://nadp.sws.uiuc.edu/sites/ntnmap.asp>) and the European Monitoring and Evaluation Programme (EMEP) for Europe (<http://www.nilu.no/projects/ccc/emepdata.html>), as well as data from Docksta, Sweden, obtained from IVL Swedish Environmental Research Institute ([www.ivl.se/english/startpage](http://www.ivl.se/english/startpage)). The measurements in Docksta are performed by IVL and are part of the national environmental monitoring program in Sweden, financed by the Swedish Environmental Protection Agency ([www.swedishepa.se](http://www.swedishepa.se)).

Records were selected for inclusion in this study from sites that (1) had anion–cation balances such that anions were within 15 % of cations, and (2) had no obvious errors in reported values attributable to sampling or laboratory analysis error. All records submitted to EMEP for all participating European countries were examined for inclusion in this study; records in the United States were selected to find sites that could represent the Northeast, Southeast, upper Midwest, Southwest, and Pacific Northwest. The resulting sites included NADP sites in 14 US states (Arizona, California, Colorado, Georgia, Michigan,

Minnesota, North Carolina, New Hampshire, New York, Ohio, Oregon, Pennsylvania, Washington, and West Virginia), and 15 European countries (Austria, Czech Republic, Finland, France, Germany, Great Britain, Latvia, Netherlands, Norway, Poland, Portugal, Russia, Spain, Sweden, and Switzerland) (Fig. 1). In some cases (Netherlands, Poland, Spain) records from two sites were combined, when stations were close to one another and had apparently been moved (Table 1).

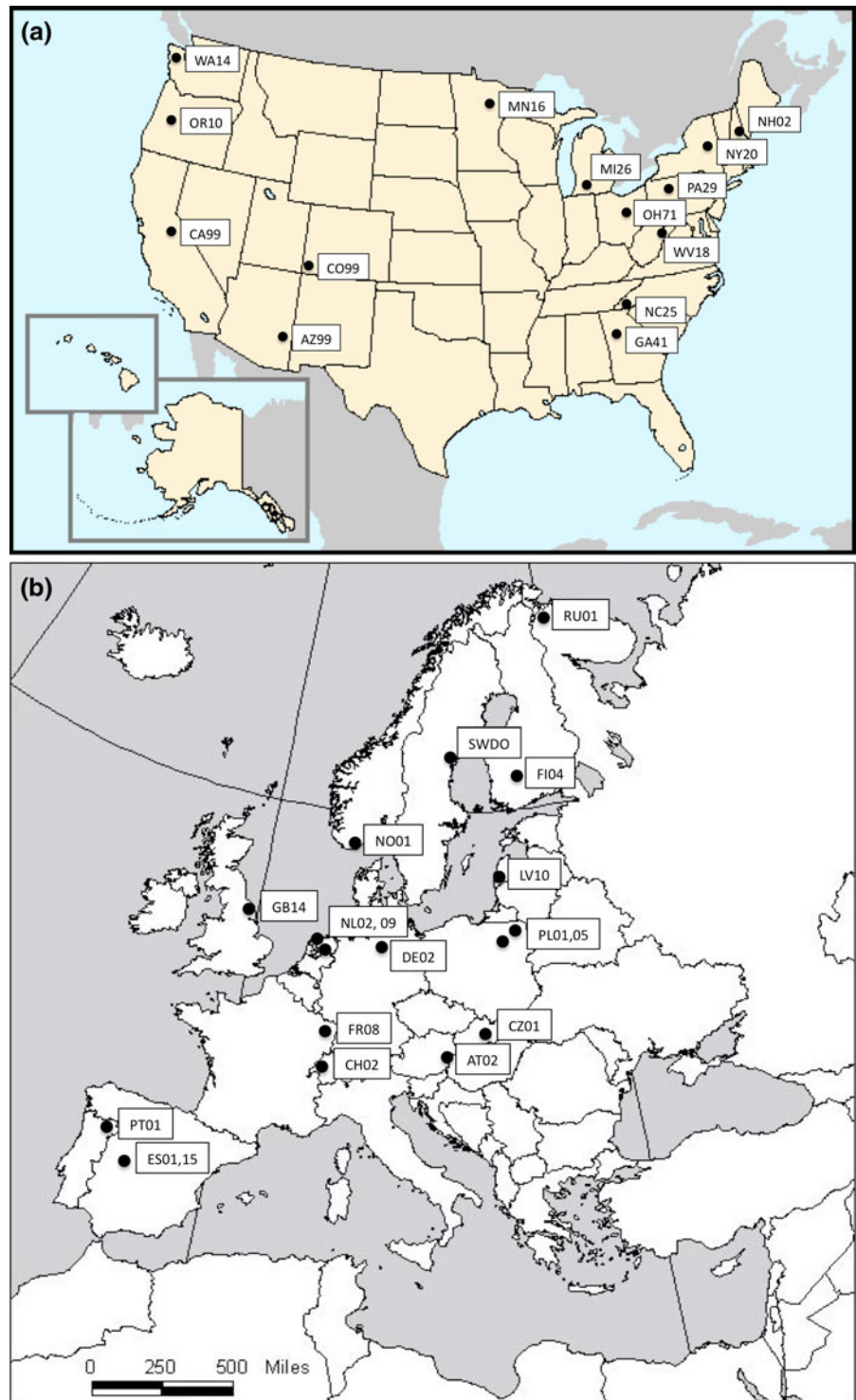
Anions and cations were closely balanced in most US states and European countries whose records were initially selected (Fig. 2). Standard errors were quite large for anions and cations in the Netherlands, and for cations in Austria, Portugal, and Russia, where cations were more than 15 % higher than anions (Fig. 2a). Anions and cations were lower, and less variable, in the US (Fig. 2b). Thus, data from Austria, France, Portugal, and Russia were included in only some of the analyses.

### Emissions controls

Since 1975, economic trends and changes in emission standards and technology have produced regionally varying trends in global SO<sub>2</sub> emissions (Smith et al. 2011). Given that electricity generation since 1970 has been responsible for 50–67 % of all SO<sub>2</sub> emissions (Taylor et al. 2005; Smith et al. 2011), controls on power plant emissions should have significant implications for precipitation chemistry. Precipitation acidity also would be expected to respond to measures to reduce SO<sub>2</sub> emissions (including using low S coal, washing coal, using scrubbers and other filter control technology, and switching to natural gas or other energy sources).

In the US, the Clean Air Act was passed in 1963 with significant amendments in 1970 and 1990 that regulated and reduced emissions, and concentrations of sulfate in receiving waters of the eastern United States declined (Driscoll et al. 1989; Likens et al. 1996). However, it was not until the 1970 Amendment that EPA established air quality standards, which led to the improvement of flue gas desulfurization (FGD) systems. Electrostatic precipitators (ESP) or bag houses collect dry salts and fly ash. In older plants, about 10 % of fly ash was emitted; in newer systems, <0.5 % of fly ash is emitted. Phase I of the Clean Air Act Amendment of 1990 required SO<sub>2</sub> emission

**Fig. 1** **a** Locations of fifteen sites in Europe with long-term precipitation chemistry records used in this study. Records are from the EMEP Program (European Monitoring and Evaluation Programme) (<http://www.nilu.no/projects/cc/sitedescriptions/index.html>) and from IVL Swedish Environmental Research Institute ([www.ivl.se/english/startpage](http://www.ivl.se/english/startpage)). Site abbreviations follow the EMEP system except for Sweden where the site is abbreviated using the *first two letters* of the station name. **b** Locations of sites in the United States with long-term precipitation chemistry records used in this study. Records are from the National Atmospheric Deposition Program (NADP, <http://nadp.sws.uiuc.edu/sites/ntnmap.asp>). Site abbreviations follow NADP conventions. See Table 1



compliance by 1995, but only for a limited number of existing plants and new construction. Phase II limited emissions at even lower levels and required compliance

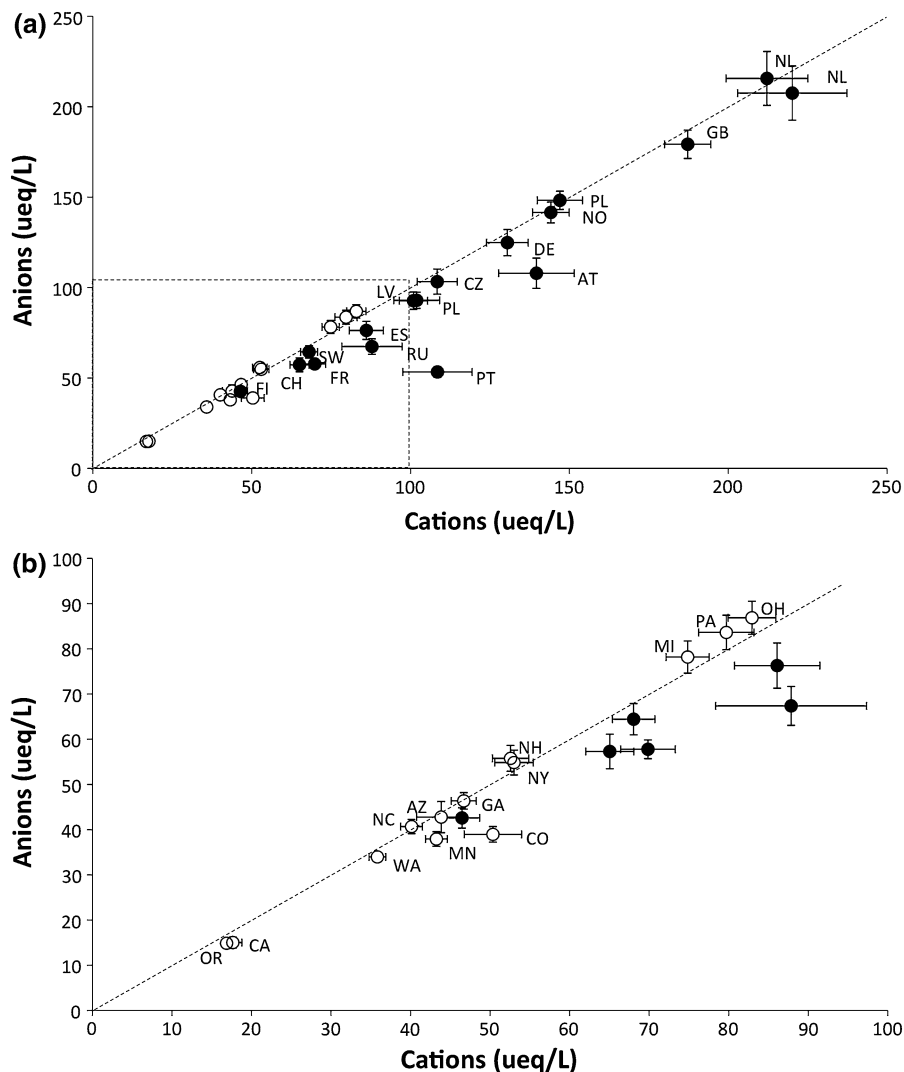
by 2000, with regulation extended to smaller units as well. Older and less regulated plants are being decommissioned, and plants are switching to alternate and

**Table 1** Average values of pH, Ca, SO<sub>4</sub>-S, NO<sub>3</sub>-N, and NH<sub>4</sub>-N in precipitation in 14 sites in the United States and 15 sites in Europe, from NADP (US) and EMEP (Europe) records for periods before and since 1990

State/Country	Site name	Code	pH		Ca		SO <sub>4</sub> -S		NO <sub>3</sub> -N		NH <sub>4</sub> -N	
			<1990	≥1991	<1990	≥1991	<1990	≥1991	<1990	≥1991	<1990	≥1991
United States												
Arizona	Oliver Knoll	AZ99 <sup>a</sup>	4.8	5.0	9.9	10.8	30.3	17.4	12.5	15.3	8.9	14.0
California	Yosemite Nat. Park	CA99	5.4	5.5	2.8	1.9	7.1	4.0	9.3	6.1	8.6	7.4
Colorado	Mesa Verde Nat. Park	CO99	4.8	5.0	24.8	18.0	26.6	17.2	16.2	16.6	7.2	9.5
Georgia	Pike County	GA41	4.6	4.7	4.7	3.2	34.1	24.1	12.4	11.1	9.2	11.8
Michigan	Kellogg Biol. Sta.	MI26	4.3	4.6	12.3	9.6	62.5	37.6	31.2	25.5	24.3	24.8
Minnesota	Marcell Exp. For.	MN16	5.0	5.2	11.1	9.2	25.8	15.8	17.7	15.4	19.1	20.0
North Carolina	Coweeta Exp. For.	NC25	4.6	4.7	3.6	2.8	30.7	21.2	11.5	10.2	7.5	8.0
New Hampshire	Hubbard Brook Exp. For.	NH02	4.4	4.5	4.0	2.5	40.6	25.3	23.0	17.4	9.0	8.9
New York	Huntington	NY20	4.4	4.6	5.0	3.4	41.9	25.8	23.7	18.0	11.2	10.1
Ohio	Wooster	OH71	4.2	4.4	10.0	8.5	70.9	47.1	29.6	24.6	21.5	21.8
Oregon	H.J. Andrews Exp. For.	OR10	5.4	5.3	1.7	1.3	5.1	3.4	2.0	2.1	1.1	1.1
Pennsylvania	Kane Exp. For.	PA29	4.2	4.3	6.5	5.0	66.7	44.3	30.4	23.4	14.9	14.0
Washington	Olympic Nat. Park	WA14	5.4	5.3	2.1	1.8	6.4	5.1	1.2	1.6	0.9	0.8
West Virginia	Fernow Exp. For.	WV18	4.2	4.4	9.3	5.9	63.3	39.2	26.2	20.2	12.6	11.7
Europe												
Austria	Illmitz	AT02 <sup>a</sup>	4.6	5.1	119.4	52.1	110.0	52.3	51.9	35.9	75.0	53.8
Czech Repub	Svratouch	CZ01	4.3	4.7	29.8	16.0	131.7	51.1	47.1	36.2	65.8	50.2
Finland	Ähtäri	FI04	4.5	4.7	6.7	4.2	43.7	18.8	21.0	16.5	21.4	12.4
France <sup>b</sup>	Donon	FR08	4.9	4.9	8.9	8.9	89.7	23.7	22.2	22.2	31.6	31.6
Germany	Langenbrügge	DE02	4.3	4.8	26.9	19.3	89.7	42.1	55.1	42.4	61.4	48.2
Latvia	Rucava	LV10	4.5	4.7	32.9	20.9	63.1	38.2	40.4	32.9	29.8	30.4
Netherlands	Witteveen, Kollumerwaard	NL02_09	4.6	5.2	17.0	19.9	97.7	50.3	44.5	34.0	88.4	59.0
Norway	Birkenes	NO01	4.3	4.6	9.1	5.7	67.9	35.8	38.8	32.5	40.9	28.3
Poland	Suwalki, Diabla Gora	PL01_05	4.4	4.7	32.9	16.4	115.2	46.3	41.4	33.4	77.8	40.9
Portugal	Braganca	PT01 <sup>a</sup>	5.4	5.6	28.2	58.4	32.7	21.7	8.4	9.7	16.7	19.6
Russia	Janiskoski	RU01	4.8	4.9	34.7	12.8	44.0	26.8	5.3	6.0	5.6	9.7
Spain	Toledo, Risco Llano	ES01_15	5.5	6.0	32.1	29.1	26.7	34.7	14.1	20.4	13.0	23.0
Sweden	Docksta	SWDO	4.4	4.7	7.3	6.8	53.2	26.4	22.6	18.6	26.2	17.7



**Fig. 2 a** Long-term average in cations and anions in study US states (*open symbols*) and European countries (*closed symbols*), with standard errors. **b** Detail of long-term average in cations and anions. Site abbreviations are from Fig. 1. European countries are *AT* Austria, *CH* Switzerland, *CZ* Czech Republic, *DE* Germany, *ES* Spain, *FI* Finland, *FR* France, *GB* Great Britain, *LV* Latvia, *NL* Netherlands, *NO* Norway, *PL* Poland, *PT* Portugal, *RU* Russia, and *SW* Sweden. States are *AZ* Arizona, *CA* California, *CO* Colorado, *GA* Georgia, *MI* Michigan, *MN* Minnesota, *NH* New Hampshire, *NY* New York, *NC* North Carolina, *OH* Ohio, *OR* Oregon, *PA* Pennsylvania, and *WA* Washington

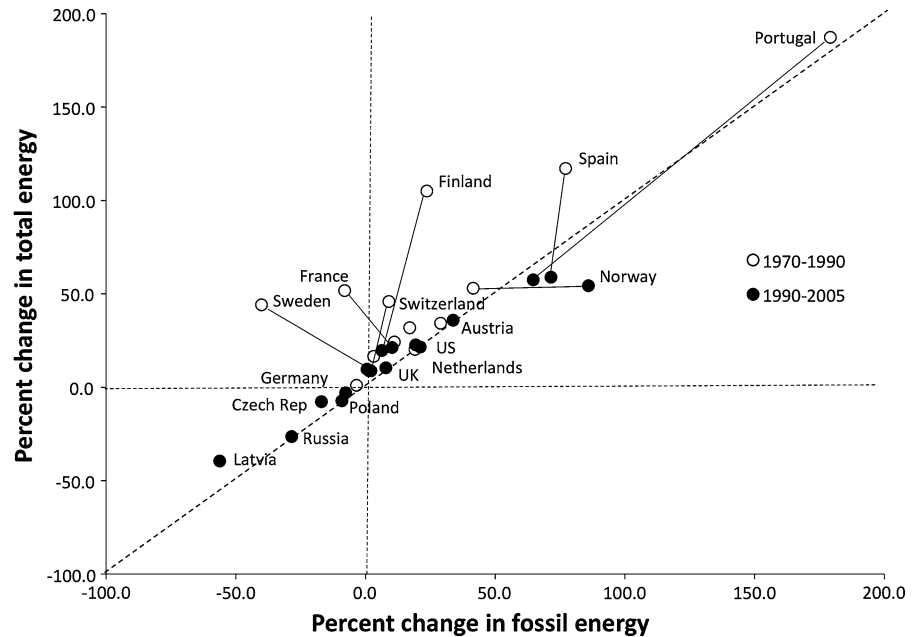


fuel combustion (power generation, industrial fuel consumption) contributing less than half that of mobile sources. The widespread adoption and subsequent continuing improvement of the 3-way catalytic converter for automobiles has reduced emissions since the mid 1990s (Medhi 2009). In the US, automobile “Tier 2” standards began in 2004, requiring an 80–90 % reduction in automobile  $\text{NO}_x$ . A 90 percent reduction of  $\text{NO}_x$  emissions from new diesel trucks began in 2007, with similar requirements for off-road diesel equipment beginning in 2010. In addition, The Clean Air Act Amendments of 1990 required major stationary sources of  $\text{NO}_x$  to install and operate reasonably available control technology (RACT) by 1995, and

the Ozone Transport Commission (OTC) developed a cap and trade  $\text{NO}_x$  Budget Program. In New England, these regulations have reduced  $\text{NO}_x$  from stationary sources by more than 50 % from 1990 levels (EPA 2006). Although the US pioneered both the technology and the regulation of  $\text{NO}_x$  emissions from automobiles, Japan, Germany, and the European Union gradually imposed very similar standards to those of the US. In Europe, the National Emission Ceilings Directive specifies  $\text{NO}_x$  emission ceilings for Member States. Since 1990, the largest reductions of emissions have occurred in the road transport sector in spite of the general increase in activity, and overall,  $\text{NO}_x$  emissions have decreased by 42 % between 1990 and 2010.



**Fig. 3** Percent change in total energy as a function of percent change in fossil energy in European countries and the United States from 1970 to 1990 (open symbols) and 1990 to 2005 (closed symbols). (Source: [http://earthtrends.wri.org/country\\_profiles/index.php?theme=6](http://earthtrends.wri.org/country_profiles/index.php?theme=6))



### Energy consumption trends

The countries chosen for this analysis had differing patterns of energy use, partially explaining the patterns in deposition of S and N over time (Earthtrends 2003) (Fig. 3). From 1970 to 1990, total energy use increased in all countries examined. Changes in total energy consumption were somewhat related to changes in fossil energy consumption for the 14 European countries and the United States ( $y = 0.83x + 31.6$ ,  $R^2 = 0.71$ ) with several notable exceptions where changes in fossil fuel consumption were less than total energy growth. From 1970 to 1990, France and Sweden reduced use of fossil fuels, largely through widespread adoption of nuclear power; Finland increased use of biomass and forestry products for energy generation. Switzerland and Spain increased fossil energy use, but total energy increased more rapidly, through development of other sources (e.g. nuclear energy).

In contrast, from 1990 to 2005, changes in fossil energy consumption explained almost all changes in total energy consumption for the 14 European countries and the United States ( $y = 0.75x + 5.4$ ,  $R^2 = 0.95$ ). During this period, there has been no significant substitution away from fossil energy sources. Five countries (Germany, Poland, Czech Republic, Latvia, and Russia) experienced declining

use of total energy and fossil fuel energy. Fossil fuel use trends were more negative than total energy trends in Latvia, Czech Republic, Finland, Sweden, and France, indicating a slight switch away from fossil energy toward alternative sources (nuclear, and to a lesser extent hydroelectric and biomass). Fossil fuel use increased faster than total energy use in Portugal, Spain, and Norway, indicating a switch toward fossil energy sources and a declining share of nuclear and renewable contributions to total energy use.

### Methods

#### Data collection

#### Precipitation chemistry

For each site, annual average records were obtained for all cations and anions, but most analyses focused on  $H^+$ ,  $SO_4-S$ ,  $NH_4-N$ ,  $NO_3-N$ , and Ca. We chose to focus on Ca because it is very sensitive to industrial and power plant emissions, and it is not as sensitive to changes in sea salt inputs as Na, for example. In addition, Ca is a more accurate proxy of basic contributions to atmospheric deposition (e.g. carbonates and oxides/hydroxides) than are other cations, which generally enter the atmosphere as salts. Records

from EMEP were obtained in units of g/mL of precipitation and converted to  $\mu\text{eq/L}$ . Records from NADP were obtained in precipitation-weighted  $\mu\text{eq/L}$  (Appendix Table 9).

We used concentrations of wet-only deposition to estimate trends in inputs over time. We recognize that dry deposition inputs can contribute substantial amounts of both S and N to ecosystems, and that the importance of dry inputs as a percentage of total inputs will vary greatly depending on location. Wet-only deposition of cations will likely be substantially lower than total inputs, and especially prone to underestimation of cation inputs in areas heavily influenced by dust deposition. Nevertheless, wet-only input estimates are more appropriate for the examination of long-term trends because (1) dry deposition inputs cannot yet be measured accurately; (2) modeling of dry inputs is complex (Elliott et al. 2009); and (3) simple measures of wet-only deposition of N and S are correlated to more complex estimates that include dry deposition (e.g. Lovett and Lindberg 1993; Brown and Froemke 2012). Thus, relative trends in deposition inputs probably can be inferred across sites using wet-only data.

Sites had varying amounts of missing data. Data for Ca from some sites (Austria, Portugal, Colorado) were excluded from analyses because of apparent errors in sampling or laboratory analysis detected using anion-cation balances. Selected outliers were omitted from analyses for some sites: 1981 for Arizona; 1985, 1991, 1996, 2002, 2009 for Ca in Colorado; 1979 for  $\text{H}^+$  for Czech Republic.

We did not use any data on cations in precipitation before 1979, and we believe that all European cation data should be regarded with caution before 1981. Dr. Lennart Granat, an author on the Hedin et al. (1994) paper, recently demonstrated that early data on cations in precipitation in Sweden are up to two times too high based on comparisons of samplers used in the European Air Chemistry Network (EACN) versus samplers that were not subject to contamination by soil components (L. Granat personal communication). The EACN samplers were gradually replaced with better samplers in the late 1970s and early 1980s. Similarly, although the US NADP database begins in 1979 for many sites, cation data before 1981 were likely compromised due to contamination from sample containers that were used at the time (Van Bowersox and Tom Butler, personal communication).

### Energy consumption

For each country in the analysis, data on energy consumption were obtained from the Earthtrends project of the World Resources Institute (Earthtrends 2003). Data on annual fossil fuel consumption and total energy consumption (thousands of tons of oil equivalent, ktoe) were obtained for 1970, 1990, and 2005. Percent changes in fossil energy and total energy, 1970–1990 and 1990–2005 were calculated.

### Data analysis

Data were analyzed using means, standard errors, and trends. Trends were determined by fitting linear regression models to data. Slope values from fitted linear models were used as estimates for rates of change. For each ion and site, trend models were fitted for the period up to 1990, 1991 to the end of the record, and for the whole period of the record. We chose 1990 as the break point because this date coincides major legislative changes in the US in 1991 and with breakup of the Soviet bloc in 1989 and associated economic changes and reversal of trends in  $\text{SO}_2$  emissions in Eastern Europe (Smith et al. 2011).

To quantify the varying relationship between  $\text{SO}_4\text{-S}$  and  $\text{H}^+$ , we compared the trends over time in  $\text{SO}_4\text{-S}$  to trends in  $\text{H}^+$ . For each US state or European country the trend in  $\text{SO}_4\text{-S}$  and  $\text{H}^+$  was determined from slope term of a linear regression predicting concentration of the element (in  $\mu\text{eq/L}$ ) versus year. Trends were defined as stoichiometric for a given country or state if  $\text{SO}_4\text{-S}$  and  $\text{H}^+$  had equal slope terms from regressions over time. The degree of stoichiometry for (1) all US states and (2) all European countries was quantified in turn by fitting a regression model to data comprising trend rates (i.e., regression slope terms) for  $\text{SO}_4\text{-S}$  versus  $\text{H}^+$ . If these regression models had a slope near 1, it indicated that trends in  $\text{SO}_4\text{-S}$  and  $\text{H}^+$  were stoichiometric for this group of European countries or US states; if not, they were not.

To test the hypothesis that trends in either Ca or  $\text{NH}_3$  must be considered in order to explain trends in  $\text{H}^+$  in precipitation, we corrected the trends over time in  $\text{SO}_4\text{-S}$  or  $\text{H}^+$ , as follows. To test how trends in Ca affected the stoichiometry of trends in  $\text{SO}_4\text{-S}$  and  $\text{H}^+$ , we compared the trend in  $\text{H}^+$  to the trend over time in Ca subtracted from the trend over time in  $\text{SO}_4\text{-S}$ . This is equivalent to adjusting the  $\text{SO}_4\text{-S}$  in precipitation in each year by

subtracting the Ca in precipitation in that year, assuming that the Ca counteracts the effect of  $\text{SO}_4\text{-S}$  on precipitation pH. These adjusted trends (trends in  $\text{SO}_4\text{-S}$  adjusted for trends in Ca) were compared to trends in  $\text{H}^+$  using the regression slope terms for comparable periods for each country or US state. The effect of adjusting for trends in Ca on trends in  $\text{H}^+$  was then tested (as for  $\text{SO}_4\text{-S}$  and  $\text{H}^+$  above) for (1) all US states and (2) all European countries by fitting a regression model to data comprising trend rates for  $\text{SO}_4\text{-S}$  adjusted for Ca versus  $\text{H}^+$ . We repeated this process to test how trends in  $\text{NH}_3$  and  $\text{NO}_3$  affected the stoichiometry of trends in  $\text{SO}_4\text{-S}$  and  $\text{H}^+$ . We fitted regression models explaining the trends in  $\text{NH}_4\text{-N}$  and  $\text{H}^+$  based on trends in  $\text{NO}_3\text{-N}$  and  $\text{SO}_4\text{-S}$ .

## Results

### Atmospheric chemistry and trends

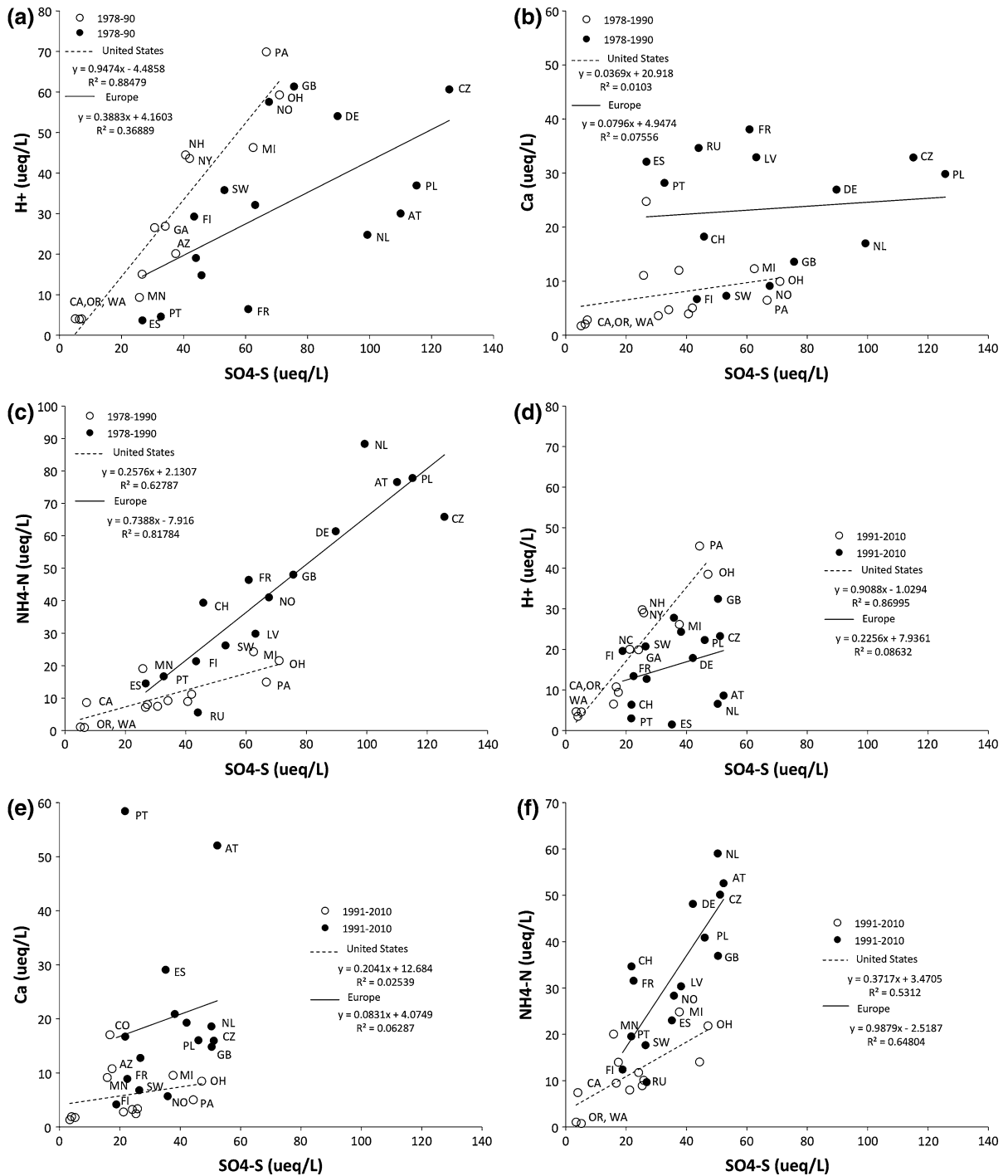
Before 1990, precipitation pH was lowest, and  $\text{SO}_4\text{-S}$  was highest, in the northeastern United States and northern and central Europe study sites (Table 1). In the US, average pH of precipitation was as low as 4.2 (Ohio, Pennsylvania, and West Virginia), 4.3 (Michigan), or 4.4 (New Hampshire, New York). In Europe, the lowest average pH values of precipitation were 4.2 (Britain), 4.3 (Czech Republic, Germany, Norway), and 4.4 (Poland, Sweden). Values of  $\text{SO}_4\text{-S}$ , on the other hand, were higher in eastern and central Europe than in the US. Average values of  $\text{SO}_4\text{-S}$  reached as high as 63–71  $\mu\text{eq/L}$  in Michigan, Ohio, Pennsylvania, and West Virginia, but average values of  $\text{SO}_4\text{-S}$  exceeded 95  $\mu\text{eq/L}$  in Austria, Czech Republic, the Netherlands and Poland (Table 1). Thus, before 1990  $\text{SO}_4\text{-S}$  in precipitation was higher in Europe than the US, controlling for pH.

Before 1990, rainfall  $\text{H}^+$  was directly related to  $\text{SO}_4\text{-S}$  in precipitation in the US and in northern Europe (Britain, Finland, Norway, Sweden (Table 1; Fig. 4a). However, in central and eastern Europe (Austria, Czech Republic, France, Germany, Poland, Netherlands)  $\text{SO}_4\text{-S}$  was higher and more variable for a given level of  $\text{H}^+$  in precipitation, compared to northern Europe and the US (Table 1; Fig. 4a). These same areas of Europe also had much higher Ca and  $\text{NH}_4\text{-N}$  in precipitation for a given levels of  $\text{SO}_4\text{-S}$  than in northern Europe or the US (Fig. 4b, c).

After 1990, precipitation became slightly less acidic in both the US and Europe, but peak  $\text{H}^+$  in the most severely affected US states was still greater than mean peak levels in Europe (Table 1). Over the period 1991–2010, average pH in precipitation in the US was as low as 4.3 (Pennsylvania), or 4.4 (Ohio, West Virginia). In contrast, the lowest average pH values in precipitation in Europe were 4.6 (Norway, Britain) or 4.7 (Czech Republic, Finland, Latvia, Poland, Sweden). Values of  $\text{SO}_4\text{-S}$ , on the other hand, declined in both the US and Europe, and remained slightly higher in Europe than the US. Over the period 1991–2010, average values of  $\text{SO}_4\text{-S}$  reached as high as 38–47  $\mu\text{eq/L}$  in Michigan, Ohio, Pennsylvania, and West Virginia, but average values of  $\text{SO}_4\text{-S}$  exceeded 50  $\mu\text{eq/L}$  in Austria, Britain, Czech Republic, and the Netherlands (Table 1). In summary, the pre-1990 pattern persisted after 1990: the most acidic precipitation and the highest  $\text{SO}_4\text{-S}$  in precipitation were concentrated in the northeast US and in central and northern Europe, but precipitation was more acidic in the northeast of the US than in the most-affected parts of Europe, despite lower  $\text{SO}_4\text{-S}$  in precipitation in the northeast US compared to Europe.

After 1990, rainfall acidity remained directly related to  $\text{SO}_4\text{-S}$  in precipitation in the US and in northern Europe (Britain, Finland, Norway, Sweden (Table 1; Fig. 4d). However, in central and eastern Europe (Austria, Czech Republic, Germany, Poland, Netherlands, as well as Portugal and Spain)  $\text{SO}_4\text{-S}$  was higher and more variable for a given level of  $\text{H}^+$  in precipitation, compared to northern Europe and the US (Table 1; Fig. 4d). As in the earlier time period, these same European countries had significantly higher levels of Ca and  $\text{NH}_4\text{-N}$  relative to  $\text{SO}_4\text{-S}$  (Fig. 4e, f).

From 1978 to 2010, concentrations of  $\text{H}^+$ ,  $\text{SO}_4\text{-S}$ , and  $\text{NO}_3\text{-N}$  declined in almost all European countries and states in the US, and  $\text{NH}_4\text{-N}$  declined in most European countries, but Ca did not decline consistently (Fig. 5). Even in locations where values of  $\text{H}^+$  were quite low in the late 1970s (e.g. Oregon, Washington, Portugal, Spain) the concentration of  $\text{H}^+$  declined significantly from 1978 to 2010 ( $p < 0.01$  for all countries and states except Latvia,  $p < 0.03$  and Portugal,  $p < 0.05$ ) (Fig. 5a, b; Table 2). From 1978 to 1990, relatively few states or countries (e.g. Arizona, Colorado, Michigan, Austria, Germany, Norway, Russia) experienced significant declines in  $\text{H}^+$  (Fig. 5a, b; Table 2). From 1991 to 2010, most state and countries



experienced significant declines in  $\text{H}^+$ ;  $\text{H}^+$  did not change significantly in Oregon, Washington, Austria, France, Latvia, Portugal, and Russia (Fig. 5a, b; Table 2). In summary, precipitation pH did not decline in very many locations before 1990, but after 1990

precipitation became significantly less acid throughout the US (except the Pacific Northwest, where precipitation was not acidic) and parts of Europe.

Even in locations where values of  $\text{SO}_4\text{-S}$  were quite low in the late 1970s (e.g. California, Oregon,

◀ **Fig. 4** Relationship between average  $\text{SO}_4\text{-S}$  and  $\text{H}^+$  (a), (d), Ca (b), (e), and  $\text{NH}_4\text{-N}$  (c), (f) in precipitation before (a–c) and after 1990 (d–f) in Europe (closed circles, solid line) and the US (open circles, dashed line) a  $\text{H}^+$  and  $\text{SO}_4\text{-S}$ , 1978–1990.  $\text{H}^+$  was closely related to  $\text{SO}_4\text{-S}$  in the US ( $r^2 = 0.88$ ) and almost 1:1, but in Europe  $\text{SO}_4\text{-S}$  values were more variable and considerably higher than  $\text{H}^+$  ( $r^2 = 0.37$ ). b Ca and  $\text{SO}_4\text{-S}$ , 1978–1990. Ca in precipitation was much higher in Europe than in the US, except for northern Europe (FI, NO, SW, GB). c  $\text{NH}_4\text{-N}$  and  $\text{SO}_4\text{-S}$ , 1978–1990.  $\text{NH}_4\text{-N}$  in precipitation was much higher in Europe, and more closely related to  $\text{SO}_4\text{-S}$  ( $r^2 = 0.82$ ) than in the US ( $r^2 = 0.63$ ). d  $\text{H}^+$  and  $\text{SO}_4\text{-S}$ , 1991–2010.  $\text{H}^+$  was closely related to  $\text{SO}_4\text{-S}$  in the US ( $r^2 = 0.87$ ) and near 1:1, but in Europe  $\text{SO}_4\text{-S}$  values were considerably higher and were not related to  $\text{H}^+$  ( $r^2 = 0.09$ ). e Ca and  $\text{SO}_4\text{-S}$ , 1991–2010. Ca in precipitation in Europe was much higher in Europe than in the US, except for northern Europe (FI, FR, NO, SW). f  $\text{NH}_4\text{-N}$  and  $\text{SO}_4\text{-S}$ , 1991–2010.  $\text{NH}_4\text{-N}$  in precipitation was much higher in Europe, nearly 1:1 with  $\text{SO}_4\text{-S}$ , and more closely related to  $\text{SO}_4\text{-S}$  ( $r^2 = 0.65$ ) than in the US ( $r^2 = 0.53$ )

Washington) the concentration of  $\text{SO}_4\text{-S}$  declined significantly from 1978 to 2010 ( $p < 0.01$  for all countries and states except Spain,  $p < 0.03$  and Portugal, not significant) (Fig. 5c, d; Table 3). From 1978 to 1990, less than half of the states or countries (Arizona, Michigan, Minnesota, New Hampshire, Oregon, Pennsylvania, Washington, Finland, Netherlands, Norway, Poland, Russia) experienced significant declines in  $\text{SO}_4\text{-S}$  (Fig. 5c, d; Table 3). From 1991 to 2010, most state and countries experienced significant declines in  $\text{SO}_4\text{-S}$ ;  $\text{SO}_4\text{-S}$  did not change significantly in California, North Carolina, Oregon, Spain, Portugal, and Russia (Fig. 5c, d; Table 3). Thus  $\text{H}^+$  declined before 1990, but after 1991, both  $\text{SO}_4\text{-S}$  and  $\text{H}^+$  declined significantly except in the western US and southern Europe and Russia.

Trends in Ca from 1978 to 2010 were subtle at best in the US (Fig. 5e), although Ca declined significantly in Georgia, Michigan, Minnesota, New Hampshire, New York, Ohio, and Pennsylvania ( $p < 0.01$ ) (Table 4). These states include those that experienced the highest  $\text{H}^+$  in precipitation and also the greatest declines in  $\text{H}^+$  from 1978 to 2010 (Table 2). Trends in Ca were quite mixed in Europe, although Ca declined significantly in Austria, Czech Republic, Germany, Finland, Latvia, Norway, Poland, and Russia ( $p < 0.01$ ) (Fig. 5f). All of these countries (except Austria, Latvia, and Russia) had significant declines in  $\text{H}^+$  over the same period (Table 2, 4). Ca increased in Portugal ( $p < 0.04$ ) (Fig. 5f). After 1990, Ca declined only in Germany and central Europe (Austria, Czech, Latvia, Poland); Austria and Germany had significant

declines in  $\text{H}^+$  over this period (Tables 2, 4). Ca increased in Portugal and Spain (Table 4).

At the beginning of the study period,  $\text{NO}_3\text{-N}$  in precipitation was higher in some parts of Europe than in the US (Fig. 5g, h). No significant negative trends in  $\text{NO}_3\text{-N}$  were detected in the US or Europe before 1990. However,  $\text{NO}_3\text{-N}$  declined, though less steeply than  $\text{SO}_4\text{-S}$ , in the mid-Atlantic and northeast of the US after 1990 (Table 5, Fig. 5g), while trends in  $\text{NO}_3\text{-N}$  in Europe were significantly negative for all countries except southern and northern Europe and Austria (Table 5; Fig. 5h).

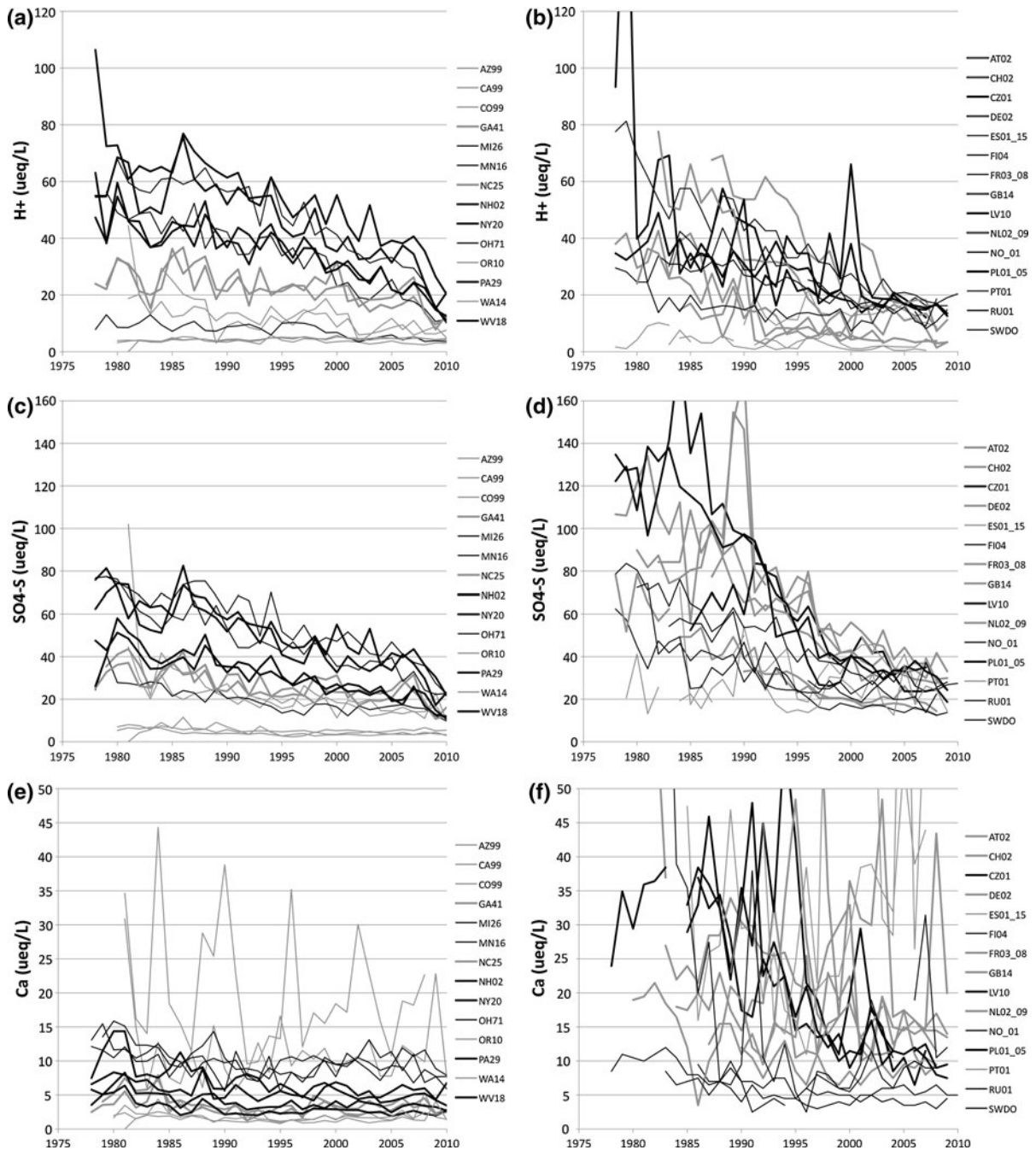
$\text{NH}_4\text{-N}$  in precipitation was generally significantly higher in Europe than the US (Fig. 5i, j). The highest  $\text{NH}_4\text{-N}$  levels in Europe (60–90  $\mu\text{eq/L}$ , Table 1) were four times as high as the highest levels in the US (15–25  $\mu\text{eq/L}$ , Table 1).  $\text{NH}_4\text{-N}$  declined significantly over the period 1978–2010 in most European countries, while trends in the US were either flat or increased slightly (Table 6).

In the US,  $\text{SO}_4\text{-S}$  was generally higher than  $\text{NH}_4\text{-N}$ , although concentrations (in  $\mu\text{eq}$ ) tended to converge as levels of  $\text{SO}_4\text{-S}$  were reduced. In Europe, however, several countries (Austria, Czech Republic, Germany, Netherlands, Poland, Switzerland) reached the cross-over point ( $\text{NH}_4\text{-N}$  greater than  $\text{SO}_4\text{-S}$ ) in the late 1990s or early 2000s, and most countries show converging patterns. In general, countries with high significant agricultural activity and thus high  $\text{NH}_3$  emissions have reached near equal  $\text{SO}_4\text{-S}$  and  $\text{NH}_4\text{-N}$  concentrations since 2000.

Factors explaining trends in atmospheric chemistry

#### Trends in $\text{SO}_4\text{-S}$ versus $\text{H}^+$

Trends in  $\text{SO}_4\text{-S}$  explained trends in  $\text{H}^+$  in the US, but not in Europe (Table 7; Fig. 6). Over the whole time period (1978–2010),  $\text{SO}_4\text{-S}$  increased only in Spain, and trends in  $\text{H}^+$  were flat or negative everywhere (Table 7; Fig. 6a). In the US, trends in  $\text{H}^+$  were explained by trends in  $\text{SO}_4\text{-S}$  ( $r^2 = 0.89$ ,  $p < 0.0001$ , Table 7), and the average trend in  $\text{H}^+$  was exactly consistent with the average trend in  $\text{SO}_4\text{-S}$  ( $\beta = 1.02$ ). In Europe, trends in  $\text{H}^+$  were weakly related to trends in  $\text{SO}_4\text{-S}$  ( $r^2 = 0.28$ ,  $p < 0.05$ ), and trends in  $\text{H}^+$  were much less negative than expected given trends in  $\text{SO}_4\text{-S}$  ( $\beta = 0.29$ ).



**Fig. 5** Trends from 1978 to 2010 in **a**  $H^+$  in the US, **b**  $H^+$  in Europe, **c**  $SO_4-S$  in the US, **d**  $SO_4-S$  in Europe, **e** Ca in the US, **f** Ca in Europe, **g**  $NO_3-N$  in the US, **h**  $NO_3-N$  in Europe, **i**  $NH_4-N$  in the US, **j**  $NH_4-N$  in Europe. *Line color and thickness for (a), (c), (e), (g), (i) indicates regions of the US: Northeast (New York, New Hampshire, Pennsylvania, West Virginia, heavy black lines), southeast (Georgia, North Carolina, heavy grey lines), upper Midwest (Ohio, Michigan, Minnesota, light black*

*lines), and west and southwest (Colorado, Arizona, California, Oregon, Washington, light grey lines). Line color and thickness for (b), (d), (f), (h), (j) indicates regions of Europe: eastern Europe (Czech Republic, Poland, Latvia, heavy black lines), western Europe (Austria, Britain, France, Germany, Netherlands, Switzerland, heavy grey lines), northern Europe (Finland, Norway, Russia, Sweden, light black lines), and southern Europe (Portugal, Spain, light grey lines)*

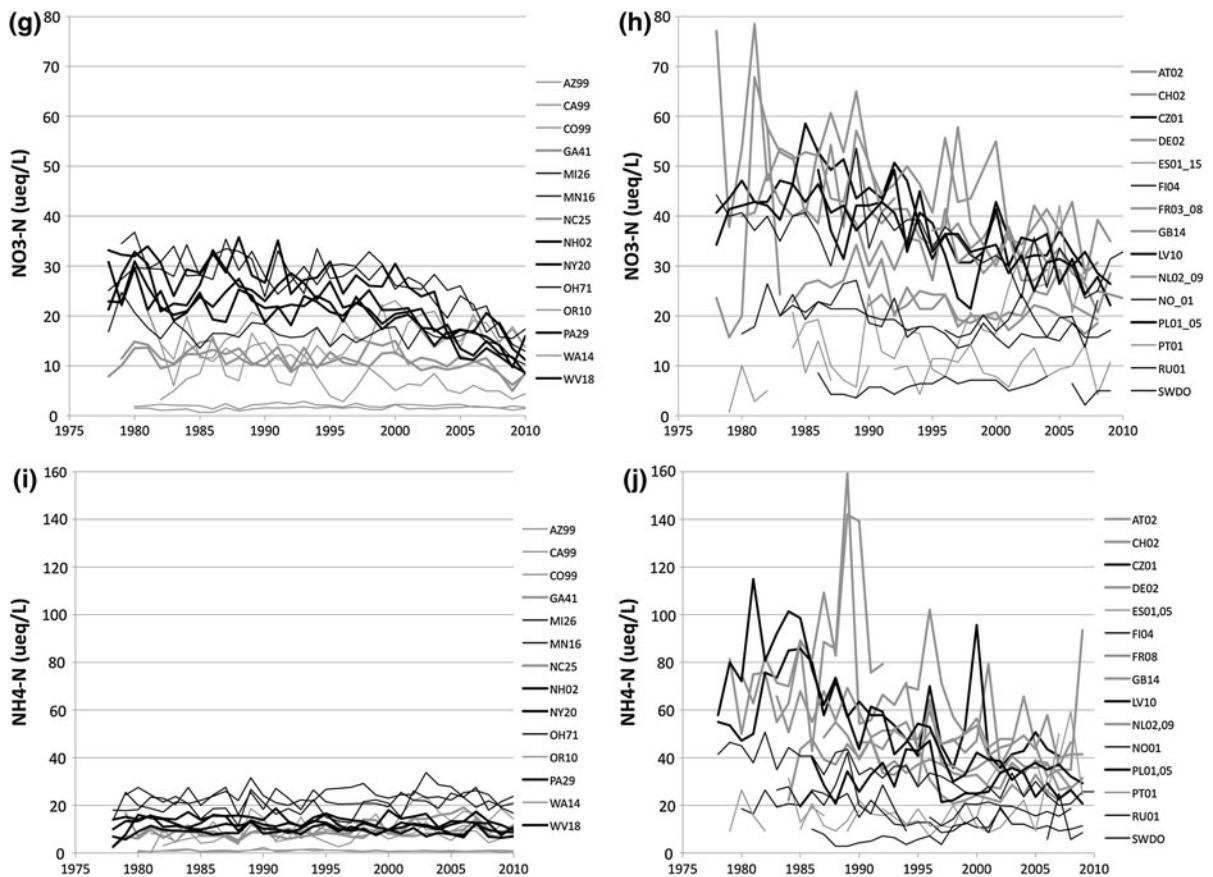


Fig. 5 continued

Taking account of trends in Ca as well as trends in  $\text{SO}_4\text{-S}$  did not help explain trends in  $\text{H}^+$  in Europe or the US from 1978 to 2010, but taking account of trends in  $\text{NH}_4\text{-N}$ , and  $\text{NO}_3\text{-N}$  did help (Table 7; Fig. 6b). Adjusting trends in  $\text{SO}_4\text{-S}$  to account for trends in Ca reduced the explanatory power of the relationship with  $\text{H}^+$  in the US ( $r^2 = 0.83$ ,  $p < 0.0001$ , Table 7), and it eliminated the significant relationship in Europe, even after removal of two outliers ( $r^2 = 0.21$ ,  $p < 0.13$ ; Table 7). In the US, trends in  $\text{H}^+$  were steeper than expected given trends in  $\text{SO}_4\text{-S}$  minus Ca ( $\beta = 1.06$ ). On the other hand, adjusting trends in  $\text{SO}_4\text{-S}$  and  $\text{H}^+$  to include trends in  $\text{NH}_4\text{-N}$  and  $\text{NO}_3\text{-N}$  slightly improved the explanatory power of the relationship in the US ( $r^2 = 0.93$ ,  $p < 0.0001$ , Table 7) and in Europe ( $r^2 = 0.67$ ,  $p < 0.0001$ , Table 7). However, trends in  $\text{H}^+$  plus  $\text{NH}_4\text{-N}$  were less steep than expected given trends in  $\text{SO}_4\text{-S}$  plus  $\text{NO}_3\text{-N}$  [ $\beta = 0.84$  (US) and  $\beta = 0.61$  (Europe)]

(Table 7). Similar results are evident for the period 1991–2010 (Table 7). Interestingly, inclusion of  $\text{NH}_4\text{-N}$  and  $\text{NO}_3\text{-N}$  did not improve the correlations among these variables in the US, but only in a few European countries (Table 8). In summary, including trends in  $\text{NH}_3$  and  $\text{NO}_3$  improved the explanation of trends in pH of precipitation in Europe, but trends in cations also were necessary to achieve stoichiometry.

#### *Changes in $\text{SO}_4\text{-S}$ in precipitation versus changes in energy consumption*

In any given year where data were available,  $\text{SO}_4\text{-S}$  in precipitation was at best weakly related to fossil fuel consumption per unit area (Fig. 7a, b, c). Before 1990, trends in  $\text{SO}_4\text{-S}$  were weakly related to trends in fossil fuel use (Fig. 7d), even though many countries had increased fossil fuel consumption but decreased  $\text{SO}_4\text{-S}$

**Table 2** Trends in H<sup>+</sup> for all years, before 1990, and since 1990, for the available record

Site	H <sup>+</sup> trend all years slope	<i>p</i> <	H <sup>+</sup> trend to 1990 slope	<i>p</i> <	H <sup>+</sup> trend after 1990 slope	<i>p</i> <	Record length
United States							
AZ99	<b>-0.66</b>	0.00	<b>-2.71</b>	0.02	<b>-0.26</b>	0.01	1981–2010
CA99	<b>-0.05</b>	0.00	-0.02	0.83	<b>-0.07</b>	0.01	1981–2010
CO99	<b>-0.32</b>	0.00	<b>-0.65</b>	0.05	<b>-0.35</b>	0.02	1981–2010
GA41	<b>-0.49</b>	0.00	-0.23	0.69	<b>-0.71</b>	0.00	1979–2010
MI26	<b>-1.29</b>	0.00	<b>-0.95</b>	0.03	<b>-1.47</b>	0.00	1979–2010
MN16	<b>-0.21</b>	0.00	-0.16	0.30	<b>-0.34</b>	0.00	1978–2010
NC25	<b>-0.38</b>	0.00	0.09	0.84	<b>-0.44</b>	0.01	1978–2010
NH02	<b>-1.03</b>	0.00	-1.01	0.08	<b>-1.47</b>	0.00	1978–2010
NY20	<b>-0.95</b>	0.00	-0.45	0.40	<b>-1.27</b>	0.00	1978–2010
OH71	<b>-1.37</b>	0.00	0.16	0.61	<b>-2.13</b>	0.00	1978–2010
OR10	<b>0.03</b>	0.00	0.08	0.07	0.01	0.67	1980–2010
PA29	<b>-1.52</b>	0.00	-1.58	0.07	<b>-1.63</b>	0.00	1978–2010
WA14	<b>0.03</b>	0.00	0.02	0.49	0.01	0.62	1980–2010
WV18	<b>-1.25</b>	0.00	0.03	0.97	<b>-1.79</b>	0.00	1978–2010
Europe							
AT02	<b>-1.07</b>	0.00	<b>-1.78</b>	0.03	0.11	0.61	1978–2009
CH02	<b>-0.57</b>	0.00	0.16	0.86	<b>-0.44</b>	0.00	1984–2008
CZ01	<b>-1.56</b>	0.00	-0.90	0.53	<b>-1.40</b>	0.00	1978–2007
DE02	<b>-2.27</b>	0.00	<b>-3.26</b>	0.03	<b>-1.23</b>	0.00	1982–2008
ES01_15	<b>-0.16</b>	0.00	-0.52	0.11	-0.09	0.20	1984–2007
FI04	<b>-0.50</b>	0.00	0.29	0.14	<b>-0.55</b>	0.00	1978–2009
FR08					-0.17	0.28	1990–2008
GB14	<b>-2.63</b>	0.00	-5.59	0.12	<b>-2.69</b>	0.00	1987–2009
LV10	<b>-0.66</b>	0.03	-0.33	0.72	-0.71	0.17	1985–2009
NL02_09	<b>-0.98</b>	0.00	-0.60	0.17	<b>-0.57</b>	0.00	1978–2009
NO01	<b>-1.71</b>	0.00	<b>-1.92</b>	0.01	<b>-1.42</b>	0.00	1978–2010
PL01_05	<b>-0.82</b>	0.00	0.30	0.63	<b>-0.84</b>	0.01	1978–2009
PT01	<b>-0.10</b>	0.05	0.04	0.94	-0.08	0.28	1983–2008
RU01	<b>-0.40</b>	0.00	<b>-1.51</b>	0.04	-0.08	0.50	1980–2009
SWDO	<b>-1.34</b>	0.00	-0.36	0.70	<b>-1.28</b>	0.00	1983–2008

Bold font indicates trend is significant at  $p < 0.01$ .  
Units are  $\mu\text{eq/L}$ .

S in precipitation. After 1990 there was no relationship between changes in SO<sub>4</sub>-S and changes in fossil fuel use (Fig. 7e), as almost all countries showed decreased SO<sub>4</sub>-S in precipitation, even with significant increases in fossil fuel use.

## Discussion

Previous research that noted long-term declines in base cation deposition in the US and Europe raised the

specter that declining cations might undermine the effectiveness of emission controls aimed to improve/reduce precipitation acidity. The purpose of our study was to extend the spatial and temporal extent of the Hedin et al. (1994) study with 20 years of additional records, and to extend the scope of the study spatially to include long-term precipitation records from more sites in the US and Europe that are variably affected by acid deposition and that have a variety of industrial and land-use histories. The sites included in our analysis were located in rural areas distant from urban



**Table 3** Trends in SO<sub>4</sub>-S for all years, before 1990, and since 1990, for the available record

Site	SO <sub>4</sub> -S trend all years Slope	<i>p</i> <	To 1990 slope	<i>p</i> <	After 1990 slope	<i>p</i> <	Record length
United States							
AZ99	<b>-1.19</b>	0.00	<b>-5.18</b>	0.04	<b>-0.36</b>	0.01	1981–2010
CA99	<b>-0.14</b>	0.00	0.23	0.47	-0.04	0.39	1981–2010
CO99	<b>-0.60</b>	0.00	-1.22	0.14	<b>-0.37</b>	0.01	1981–2010
GA41	<b>-0.61</b>	0.00	-0.91	0.09	<b>-0.49</b>	0.02	1979–2010
MI26	<b>-1.47</b>	0.00	<b>-1.55</b>	0.02	<b>-1.21</b>	0.00	1979–2010
MN16	<b>-0.54</b>	0.00	<b>-0.92</b>	0.02	<b>-0.25</b>	0.02	1978–2010
NC25	<b>-0.50</b>	0.00	-0.23	0.57	-0.33	0.08	1978–2010
NH02	<b>-0.97</b>	0.00	<b>-0.99</b>	0.02	<b>-1.12</b>	0.00	1978–2010
NY20	<b>-0.93</b>	0.00	-0.22	0.74	<b>-0.98</b>	0.00	1978–2010
OH71	<b>-1.48</b>	0.00	-0.65	0.10	<b>-1.82</b>	0.00	1978–2010
OR10	<b>-0.09</b>	0.00	<b>-0.29</b>	0.00	0.00	0.94	1980–2010
PA29	<b>-1.31</b>	0.00	<b>-1.05</b>	0.05	<b>-1.22</b>	0.00	1978–2010
WA14	<b>-0.06</b>	0.00	<b>-0.24</b>	0.01	<b>0.04</b>	0.04	1980–2010
WV18	<b>-1.43</b>	0.00	-0.74	0.33	<b>-1.52</b>	0.00	1978–2010
Europe							
AT02	<b>-3.10</b>	0.00	1.04	0.61	<b>-2.67</b>	0.00	1978–2009
CH02	<b>-1.65</b>	0.00	-1.51	0.20	<b>-1.22</b>	0.00	1984–2008
CZ01	<b>-4.75</b>	0.00	-3.87	0.07	<b>-2.82</b>	0.00	1978–2007
DE02	<b>-3.04</b>	0.00	-0.02	0.99	<b>-2.31</b>	0.00	1982–2008
ES01_15	<b>0.63</b>	0.03	4.14	0.08	0.33	0.41	1984–2007
FI04	<b>-1.38</b>	0.00	<b>-1.43</b>	0.01	<b>-0.88</b>	0.00	1978–2009
FR08					<b>-0.96</b>	0.00	1990–2008
GB14	<b>-2.19</b>	0.00	-4.93	0.28	<b>-2.17</b>	0.00	1987–2009
LV10	<b>-2.23</b>	0.00	1.91	0.35	<b>-2.66</b>	0.00	1985–2009
NL02_09	<b>-2.36</b>	0.00	<b>4.50</b>	0.02	<b>-3.01</b>	0.00	1978–2009
NO01	<b>-1.85</b>	0.00	<b>-2.05</b>	0.00	<b>-1.51</b>	0.00	1978–2010
PL01_05	<b>-3.95</b>	0.00	<b>-3.16</b>	0.00	<b>-2.77</b>	0.00	1978–2009
PT01	-0.38	0.18	1.38	0.43	0.21	0.55	1979–2008
RU01	<b>-0.99</b>	0.00	<b>-3.23</b>	0.03	-0.05	0.82	1980–2009
SWDO	<b>-1.71</b>	0.00	-1.19	0.30	<b>-1.13</b>	0.00	1983–2008

Bold font indicates trend is significant at  $p < 0.01$ .  
Units are  $\mu\text{eq/L}$ .

or agricultural areas, and had long-term records of high quality. We predicted that although general patterns of precipitation chemistry would be similar among regions due to the overall efforts of developed countries to reduce air pollution and acid rain starting in the mid-late 20th century, trends in precipitation acidity would vary among locations due to different patterns of pollution control, trends in NH<sub>3</sub>, as well as differing natural sources of cations.

Over the >30-yr period of NADP and EMEP records (1978–2010), precipitation pH and SO<sub>4</sub>-S levels declined in all US states and all European countries, with the exception of those not significantly impacted by

acidic precipitation to begin with (e.g. the Pacific Northwest in the US, Spain and Portugal in Europe). However, the relationship between SO<sub>4</sub>-S and H<sup>+</sup> differed markedly between the US and Europe. For any given level of S in precipitation, H<sup>+</sup> was lower in Europe compared to the US. We suggest that two factors can account for this observation. First, dust deposition is higher in southern/central Europe than in the US. Dust from North Africa accounts for 50–70 % of global dust emissions with Asian deserts contributing 10–25 % of the total (Ginoux et al. 2004), and is enriched in calcite with very little gypsum (Loye-Pilot et al. 1986). These natural carbonates are capable of neutralizing

**Table 4** Trends in Ca for all years, before 1990, and since 1990, for the available record

Site	Ca trend all years slope	<i>p</i> <	To 1990 slope	<i>p</i> <	After 1990 slope	<i>p</i> <	Record length
United States							
AZ99	-0.06	0.62	-1.22	0.15	0.15	0.32	1981–2010
CA99	-0.03	0.25	0.06	0.66	0.04	0.33	1981–2010
CO99	0.25	0.49	0.45	0.74	0.20	0.48	1981–2010
GA41	<b>-0.08</b>	0.00	<b>-0.27</b>	0.03	0.02	0.64	1979–2010
MI26	<b>-0.14</b>	0.00	-0.30	0.09	-0.01	0.88	1979–2010
MN16	<b>-0.08</b>	0.02	<b>-0.37</b>	0.00	<b>-0.25</b>	0.02	1978–2010
NC25	-0.03	0.14	-0.10	0.41	0.04	0.19	1978–2010
NH02	<b>-0.08</b>	0.00	<b>-0.27</b>	0.00	0.00	0.87	1978–2010
NY20	<b>-0.08</b>	0.00	-0.12	0.25	-0.01	0.69	1978–2010
OH71	<b>-0.10</b>	0.00	<b>-0.34</b>	0.01	-0.06	0.26	1978–2010
OR10	-0.01	0.57	<b>-0.08</b>	0.02	<b>0.05</b>	0.04	1980–2010
PA29	<b>-0.09</b>	0.00	<b>-0.21</b>	0.04	-0.06	0.11	1978–2010
WA14	-0.01	0.58	-0.11	0.07	<b>0.05</b>	0.00	1980–2010
WV18	<b>-0.19</b>	0.00	-0.37	0.07	<b>-0.09</b>	0.04	1978–2010
Europe							
AT02	<b>-5.71</b>	0.00	-6.84	0.50	<b>-5.60</b>	0.00	1987–2009
CH02	-0.24	0.09	-0.27	0.64	-0.44	0.10	1984–2008
CZ01	<b>-1.00</b>	0.00	<b>-4.34</b>	0.04	<b>-0.74</b>	0.02	1986–2007
DE02	<b>-0.73</b>	0.00	<b>1.25</b>	0.05	<b>-1.16</b>	0.00	1983–2008
ES01_15	0.54	0.14	0.11	0.97	<b>1.70</b>	0.00	1985–2007
FI04	<b>-0.15</b>	0.00	<b>-1.20</b>	0.01	-0.06	0.07	1986–2009
FR08					-0.03	0.70	1990–2008
GB14	0.07	0.53	-0.45	0.74	0.04	0.79	1987–2009
LV10	<b>-1.36</b>	0.00	-0.40	0.86	<b>-1.86</b>	0.00	1985–2009
NL02_09	-0.10	0.60	-0.95	0.08	-0.75	0.10	1978–2009
NO01	<b>-0.18</b>	0.00	-0.22	0.06	-0.06	0.11	1978–2010
PL01_05	<b>-1.03</b>	0.00	0.02	0.96	<b>-1.26</b>	0.00	1978–2009
PT01	<b>2.70</b>	0.04			2.67	0.11	1989–2009
RU01	<b>-1.33</b>	0.01	<b>-9.84</b>	0.00	0.16	0.70	1982–2009
SWDO	0.10	0.09	0.05	0.83	<b>0.37</b>	0.00	1983–2008

Bold font indicates trend is significant at  $p < 0.01$ .

Units are  $\mu\text{eq/L}$ .

anthropogenic acidity. Countries in Europe, which are closer to these dust sources, are more affected by alkaline dust than is the US, as indicated by our finding of higher Ca levels in precipitation in Europe than the US. Draaijers et al. (1997) calculated that up to 50 % of precipitation acidity in Europe could be neutralized by dust inputs from Saharan/Sahel sources. Second, levels of  $\text{NH}_4\text{-N}$  were substantially higher in most of Europe, implying higher emissions of  $\text{NH}_3$ , which neutralize precipitation acidity, compared to the US.

More locally derived dust can also affect precipitation chemistry, but we did not observe trends that could

be attributed to local factors. In Argentina, Piccolo et al. (1988) found that continental air masses that had traveled over alkaline soil areas were associated with high pH-precipitation (low  $\text{H}^+$ ). At the multi-century scale, Neff et al. (2008) saw a signal of increased Ca loads, indicative of increased dust, in the western US associated with increased human expansion and the expansion of livestock grazing. We expected distinctive Ca patterns in arid regions of the US, and sites subjected to local land management change. However, there were no significant trends in Ca since 1978 in any of the western states examined in this study. Moreover, known

**Table 5** Trends in NO<sub>3</sub>-N for all years, before 1990, and since 1990, for the available record

Site	NO <sub>3</sub> -N trend all years slope	<i>p</i> <	To 1990 slope	<i>p</i> <	After 1990 slope	<i>p</i> <	Record length
United States							
AZ99	<b>0.16</b>	0.03	-0.20	0.65	0.27	0.05	1981–2010
CA99	<b>-0.16</b>	0.03	<b>1.18</b>	0.04	-0.16	0.06	1981–2010
CO99	0.05	0.48	0.26	0.58	0.07	0.54	1981–2010
GA41	<b>-0.12</b>	0.01	-0.17	0.29	<b>-0.21</b>	0.02	1979–2010
MI26	<b>-0.42</b>	0.00	-0.37	0.20	<b>-0.60</b>	0.00	1979–2010
MN16	<b>-0.15</b>	0.00	-0.26	0.22	<b>-0.16</b>	0.03	1978–2010
NC25	<b>-0.08</b>	0.02	0.11	0.45	<b>-0.13</b>	0.04	1978–2010
NH02	<b>-0.44</b>	0.00	-0.52	0.08	<b>-0.76</b>	0.00	1978–2010
NY20	<b>-0.39</b>	0.00	-0.11	0.65	<b>-0.63</b>	0.00	1978–2010
OH71	<b>-0.39</b>	0.00	0.24	0.33	<b>-0.84</b>	0.00	1978–2010
OR10	-0.01	0.41	0.00	0.99	<b>-0.04</b>	0.00	1980–2010
PA29	<b>-0.52</b>	0.00	-0.28	0.26	<b>-0.89</b>	0.00	1978–2010
WA14	<b>0.01</b>	0.04	-0.01	0.88	-0.01	0.51	1980–2010
WV18	<b>-0.44</b>	0.00	-0.04	0.90	<b>-0.79</b>	0.00	1978–2010
Europe							
AT02	<b>-0.90</b>	0.00	-1.56	0.10	-0.36	0.06	1978–2009
CH02	<b>-0.43</b>	0.00	0.87	0.22	<b>-0.43</b>	0.01	1984–2008
CZ01	<b>-0.63</b>	0.00	0.54	0.15	<b>-0.78</b>	0.01	1978–2007
DE02	<b>-0.88</b>	0.00	0.26	0.71	<b>-0.90</b>	0.00	1982–2008
ES01_15	<b>0.81</b>	0.00	-0.20	0.89	<b>1.38</b>	0.00	1984–2007
FI04	<b>-0.23</b>	0.00	0.19	0.48	-0.11	0.13	1980–2009
FR08					-0.02	0.86	1990–2008
GB14	<b>-0.47</b>	0.00	-3.57	0.15	<b>-0.39</b>	0.04	1987–2009
LV10	<b>-0.94</b>	0.00	-0.93	0.72	<b>-0.80</b>	0.01	1986–2009
NL02_09	<b>-0.69</b>	0.00	0.81	0.13	<b>-1.20</b>	0.00	1978–2010
NO01	<b>-0.39</b>	0.00	0.11	0.79	<b>-0.60</b>	0.00	1978–2010
PL01_05	<b>-0.50</b>	0.00	0.10	0.70	<b>-0.68</b>	0.00	1978–2009
PT01	0.09	0.35	0.40	0.49	0.01	0.92	1979–2009
RU01	-0.01	0.89	-0.64	0.38	-0.06	0.32	1986–2009
SWDO	-0.17	0.07	0.30	0.59	0.06	0.69	1983–2008

Bold font indicates trend is significant at  $p < 0.01$ .  
Units are  $\mu\text{eq/L}$ .

patterns of logging activity in the Pacific Northwest in the last 30 years could not be discerned from precipitation data in our western states, because the slight decreases in Ca in precipitation, coincident with decreased use of logging roads, cannot be separated from the overall pattern of decreasing Ca in precipitation across the US. Also, local sources can be overwhelmed by more regional and global variations in dust deposition or industrial emissions; dust from Asia and other aerosols arriving at North American shores from overseas is comparable to average local particulate emissions (Vicars and Sickman 2011; Yu et al. 2012).

The lack stoichiometry between SO<sub>4</sub>-S and H<sup>+</sup> in precipitation differed between the US and Europe, and was attributable to broad economic or land use changes that affected emissions of alkaline dust and/or NH<sub>3</sub>, as well as to emissions controls that reduce alkaline and/or S-containing particulates, depending on the time and place. During the first time period before 1990, many US states (9 of 13 reported) and most European countries had less negative trends in H<sup>+</sup> than in SO<sub>4</sub>-S, the pattern reported by Hedin et al. (1994). This pattern was most significant in eastern European countries, a region with the highest SO<sub>4</sub>-S

**Table 6** Trends in NH<sub>4</sub>-N for all years, before 1990, and since 1990, for the available record

Site	NH <sub>4</sub> -N trend all years slope	<i>p</i>	To 1990 slope	<i>p</i>	After 1990 slope	<i>p</i>	Record length
United States							
AZ99	<b>0.30</b>	0.00	-0.30	0.60	<b>0.48</b>	0.00	1981–2010
CA99	0.00	0.97	1.38	0.04	0.03	0.80	1981–2010
CO99	<b>0.16</b>	0.00	0.21	0.51	0.17	0.07	1981–2010
GA41	<b>0.15</b>	0.01	-0.37	0.12	0.25	0.06	1979–2010
MI26	0.05	0.48	0.14	0.60	0.07	0.65	1979–2010
MN16	0.12	0.11	0.07	0.84	0.35	0.03	1978–2010
NC25	0.06	0.12	0.20	0.26	0.10	0.16	1978–2010
NH02	-0.02	0.53	0.16	0.27	-0.14	0.06	1978–2010
NY20	-0.05	0.27	0.20	0.46	-0.07	0.29	1978–2010
OH71	0.00	0.97	0.26	0.40	-0.12	0.25	1978–2010
OR10	-0.01	0.29	0.03	0.38	-0.02	0.04	1980–2010
PA29	-0.07	0.08	0.04	0.62	-0.13	0.18	1978–2010
WA14	-0.01	0.18	0.08	0.12	<b>-0.02</b>	0.01	1980–2010
WV18	-0.06	0.10	0.04	0.81	-0.09	0.23	1978–2010
Europe							
AT02	-0.85	0.08	1.55	0.51	0.03	0.96	1978–2009
CH02	<b>-0.40</b>	0.03	1.68	0.34	<b>-0.55</b>	0.02	1984–2008
CZ01	<b>-0.82</b>	0.01	1.17	0.26	-0.80	0.29	1978–2007
DE02	<b>-0.76</b>	0.00	0.29	0.82	-0.34	0.18	1982–2008
ES01_15	<b>1.24</b>	0.00	1.84	0.15	<b>1.90</b>	0.00	1984–2007
FI04	<b>-0.48</b>	0.00	0.19	0.64	<b>-0.29</b>	0.04	1980–2009
FR08					<b>-1.48</b>	0.00	1990–2008
GB14	<b>-0.69</b>	0.01	-3.36	0.33	-0.45	0.19	1987–2009
LV10	-0.35	0.13	-2.28	0.41	<b>-0.71</b>	0.03	1986–2009
NL02_09	<b>-1.47</b>	0.01	<b>6.20</b>	0.00	<b>-2.48</b>	0.00	1978–2010
NO01	<b>-0.70</b>	0.00	-0.44	0.21	<b>-0.64</b>	0.00	1978–2010
PL01_05	<b>-2.08</b>	0.00	-1.92	0.21	<b>-1.25</b>	0.00	1978–2009
PT01	0.41	0.08	-0.12	0.86	<b>1.35</b>	0.02	1979–2009
RU01	<b>0.38</b>	0.02			0.44	0.07	1986–2009
SWDO	<b>-0.41</b>	0.02	0.58	0.65	-0.01	0.96	1983–2008

Bold font indicates trend is significant at  $p < 0.01$ .  
Units are  $\mu\text{eq/L}$ .

and H<sup>+</sup> loading in Europe, and to a lesser extent, states in the US that were also most significantly impacted by acid rain. On a global basis, African dust has increased since the 1970s (Prospero and Lamb 2003) and thus is not likely to be a cause of the lack of stoichiometry and the greater declines in SO<sub>4</sub>-S than H<sup>+</sup>. Instead, in the US this period corresponds to major changes in legislation controlling particulate emissions that contain both cations and S. Similar legislation in Europe also caused non-stoichiometric declines in H<sup>+</sup> and SO<sub>4</sub>-S before 1990, although the non-stoichiometric pattern tended to extend past 1990 in the most severely

affected European countries, likely due to differences in legislation and implementation of technology between countries and continents. However, in Europe, declines in SO<sub>4</sub>-S and H<sup>+</sup> before 1990 also were related to patterns of energy use resulting from economic factors. For example, eastern European countries (Poland, Hungary, Czechoslovakia) showed sharp declines immediately after the fall of the Soviet Union, a period of declining industrial activity.

After 1990 in the US, trends in H<sup>+</sup> in the US were more negative than expected based on declines in SO<sub>4</sub>-S, the exact opposite pattern of that described by

**Table 7** Regression models relating (1) trends in  $H^+$  to trends in  $SO_4-S$ , (2) trends in  $H^+$  to trends in  $SO_4-S$  adjusted for Ca, and (3) trends in  $H^+$  plus  $NH_4-N$  to trends in  $SO_4-S$  plus  $NO_3-N$ , for 14 states in the US and 14 countries in Europe

	All years			Since 1990		
	$r^2$	Beta	$p <^a$	$r^2$	Beta	$p <^2$
United States						
$SO_4-S$ versus $H^+$	0.89	1.02	0.00	0.98	1.23	0.00
$SO_4-S$ minus Ca versus $H^+$	0.83	1.06	0.00	0.93	1.24	0.00
$SO_4-S$ plus $NO_3-N$ versus $H^+$ plus $NH_4-N$	0.93	0.84	0.00	0.98	0.89	0.00
Europe						
$SO_4-S$ versus $H^+$	0.28	0.29	0.05	0.17	0.27	0.13
$SO_4-S$ minus Ca versus $H^+$	0.08	0.13	0.32	0.22	0.27	0.08
$SO_4-S$ minus Ca versus $H^{+b}$	0.21	0.32	0.13	0.40	0.74	0.02
$SO_4-S$ plus $NO_3-N$ versus $H^+$ plus $NH_4-N$	0.67	0.61	0.00	0.66	0.71	0.00

Trends in  $H^+$  in the US are stoichiometric: they are significantly related to trends  $SO_4-S$  in all periods (1978–2010, 1978–1990, 1991–2010). The inclusion of  $NO_3-N$  and  $NH_4-N$  improves the relationship slightly for 1978–2010, but does not affect the relationship for 1991–2010. Trends in  $H^+$  in Europe are not stoichiometric: they are not significantly related to trends  $SO_4-S$  in any period. Adjusting the trends in  $SO_4-S$  to account for the trends in Ca does not provide a better explanation for trends in  $H^+$  in either the US or Europe. However, adjusting trends in Europe to account for trends in  $NO_3-N$  and  $NH_4-N$  produces a significant relationship

<sup>a</sup>  $p$ -values of beta (slope of the regression)

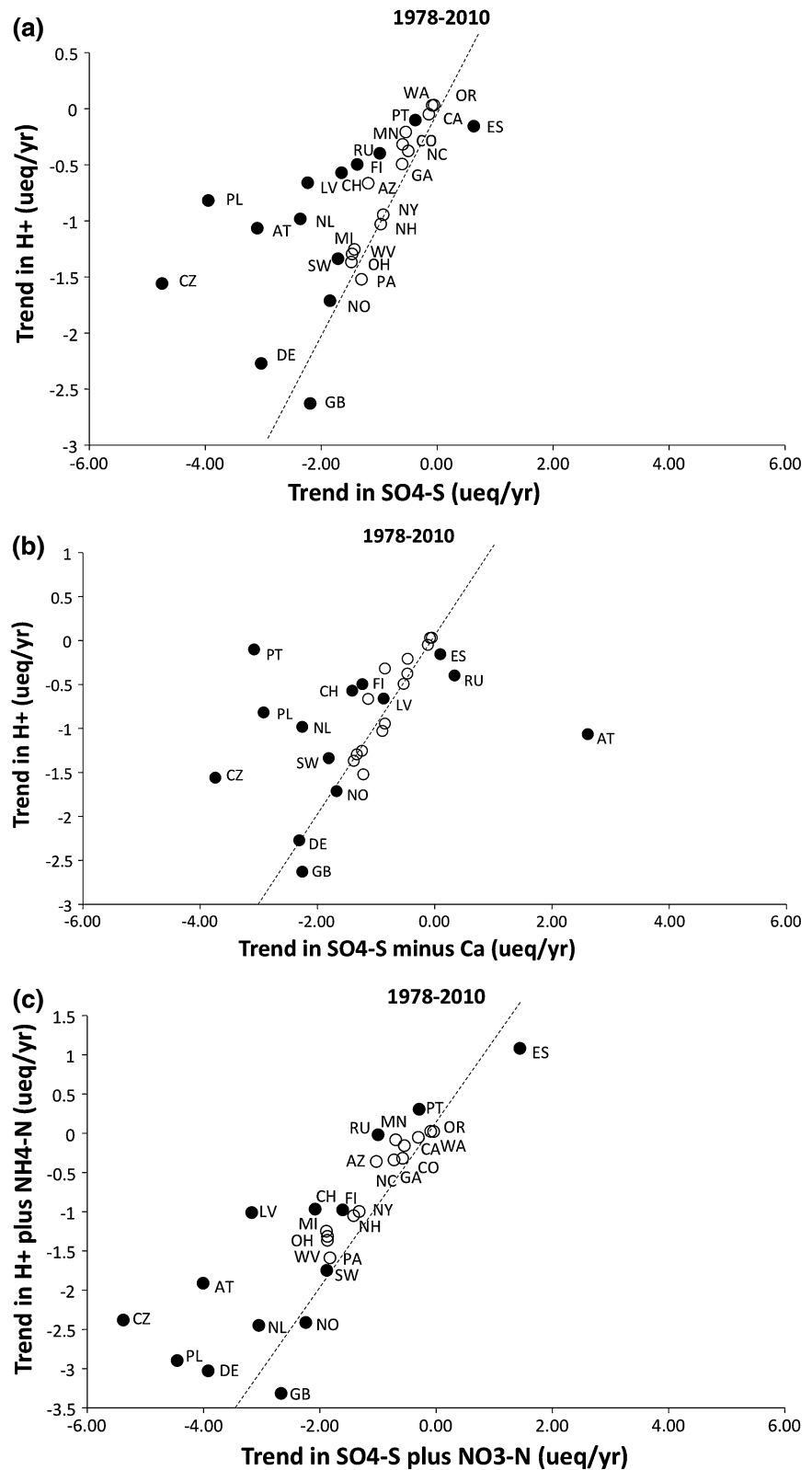
<sup>b</sup> Regression based on removal of two outliers (AT02, PT01)

Hedin et al. (1994). This cannot be explained by the legislative focus during this time frame on  $SO_2$  emissions, which would lead to stoichiometric reductions in  $H^+$ . Increasing  $NH_3$  in the atmosphere could cause this pattern, and indeed, both emissions of  $NH_3$  (and deposition of  $NH_4-N$ ) increased slightly in the midwest US (Lehmann et al. 2007), but not in most sites used in this study. Recent increases in  $NH_4-N$  loading in the US may be due to the consolidation of independent animal production and processing operations; larger and more industrial operations are known to produce larger concentrated amounts of waste with larger emission factors (Merkel 2002). However,  $NO_3-N$  in precipitation, a proxy for  $NO_x$  emissions and nitric acid deposition, declined in the US after 1990, and declines were steepest in the northeastern and midwestern states. The significant declines in  $NO_3-N$  observed in the US since 1991 are likely explained both by changes in the transportation industry (catalytic converters) and changes for industrial emissions. Adding trends in  $NO_3-N$  to trends in  $SO_4-S$  produces trends in  $H^+$  that are less steep than expected given trends in  $SO_4-S$  and  $NO_3-N$  (data not shown). Thus, trends in  $H^+$  in the US after 1990 depend on regulation of both S and N.

In contrast, trends in precipitation chemistry in Europe after 1990 appear to depend on both economic and land use trends as well as regulation of S and N emissions. After 1990, declines in  $SO_4-S$  remained steeper than  $H^+$  in many countries in Europe, especially central European countries, following the pattern described by Hedin et al. (1994), even though most European countries also had significant declines in  $NO_3-N$  in precipitation. Although particulate control measures that could reduce S-containing particulates (and cations) in deposition were still taking effect after 1990 in Europe, our analysis suggests that the non-stoichiometric trends in  $H^+$  and  $SO_4-S$  were also significantly affected by sharp declines in  $NH_3$  emissions, as well as declines in  $NO_3-N$ , across Europe. These declines can be attributed to declining agricultural activity in eastern Europe, regulation by the National Emission Ceiling Directive, and also possibly declining  $SO_2$  emissions and thus the long range transport of ammonium sulfate aerosols. This pattern is seen mostly clearly in eastern European countries, which had the steepest declines in  $NO_3-N$  and  $NH_4-N$ .

Trends in precipitation chemistry and the drivers of these changes have continued to diverge between the US and European countries since 2000. We saw

**Fig. 6** Trends in **a**  $H^+$  in precipitation as a function of trends in  $SO_4-S$  in precipitation ( $\mu eq/year$ ), in the US and European countries, **b**  $H^+$  as a function of trends in  $SO_4-S$  minus Ca, and **c**  $H^+$  plus  $NH_4-N$  as a function of trends in  $SO_4-S$  plus  $NO_3-N$ . Trends are stoichiometric if they fall on the 1:1 line (equal trends). *Points below the line* are cases in which the trend in  $SO_4-S$  is less negative or more positive than the trend in  $H^+$ , and *points above the line* are cases in which the trend in  $SO_4-S$  is more negative or less positive than the trend in  $H^+$



**Table 8** Interannual variability in precipitation chemistry

	SO <sub>4</sub> -S versus H <sup>+</sup>	SO <sub>4</sub> -S minus Ca versus H <sup>+</sup>	SO <sub>4</sub> -S plus NO <sub>3</sub> -N versus H <sup>+</sup> plus NH <sub>4</sub> -N
AZ99	0.85	0.85	0.82
CA99	0.22	0.39	0.83
CO99	0.68	0.38	0.77
GA41	0.89	0.91	0.92
MI26	0.95	0.97	0.97
MN16	0.65	0.78	0.66
NC25	0.92	0.95	0.94
NH02	0.95	0.95	0.97
NY20	0.91	0.92	0.98
OH71	0.95	0.96	0.97
OR10	-0.62	-0.48	-0.39
PA29	0.93	0.94	0.95
WA14	-0.31	-0.24	-0.09
WV18	0.97	0.98	0.98
AT02	0.58	-0.48	0.62
CH02	0.90	0.89	0.86
CZ01	0.51	0.35	<b>0.72</b>
DE02	0.92	0.88	0.95
ES01	-0.58	-0.31	<b>0.74</b>
FI04	0.93	0.55	0.97
FR08	0.26	0.37	<b>0.94</b>
GB14	0.88	0.94	0.95
LV10	0.88	0.94	0.95
NL02_09	0.37	0.31	<b>0.60</b>
NO01	0.61	0.62	<b>0.96</b>
PL01_05	0.66	0.64	<b>0.92</b>
PT01	0.07	0.14	-0.08
RU01	0.73	-0.23	0.11
SWDO	0.90	0.94	0.97

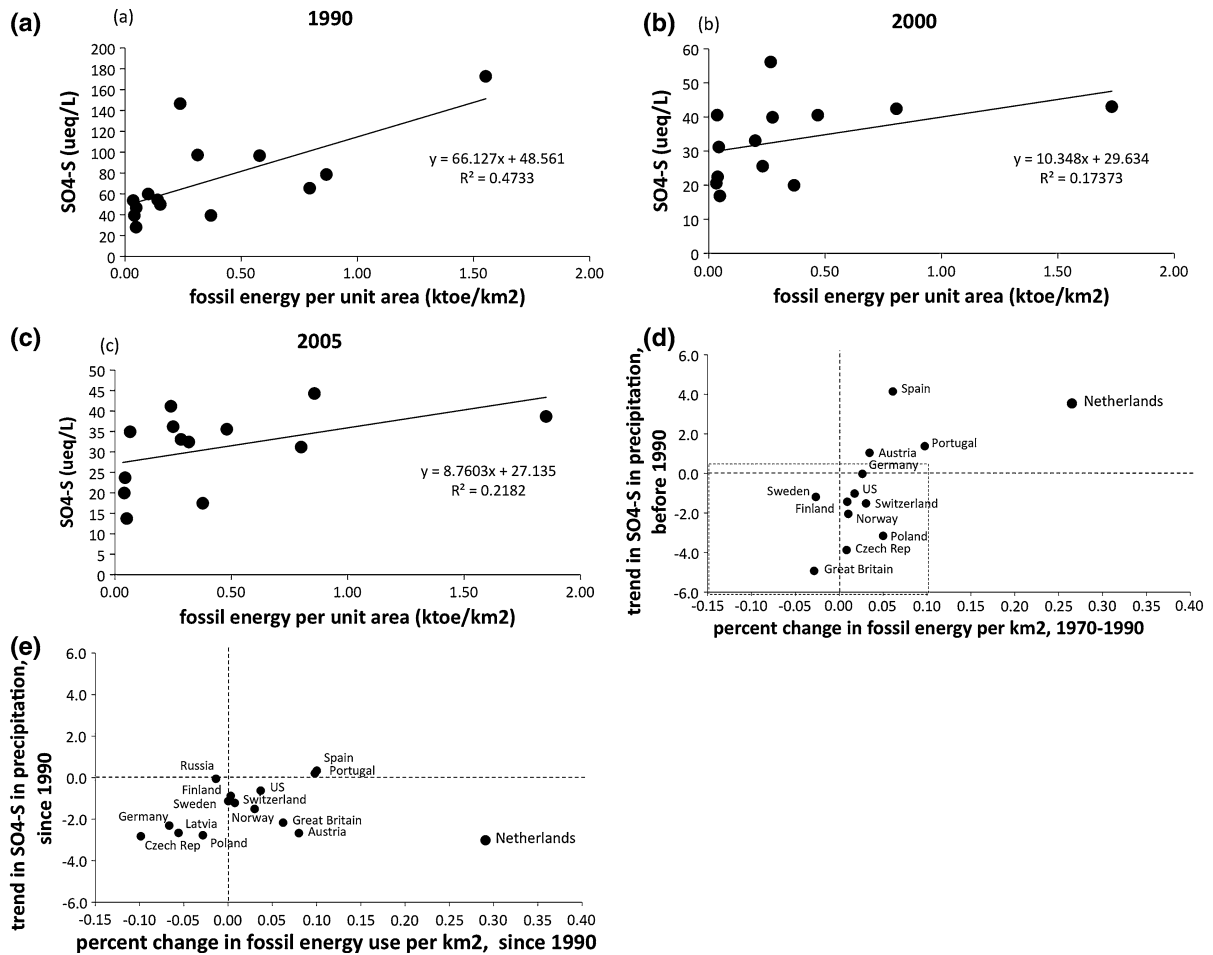
Correlations of annual values in precipitation of (1) H<sup>+</sup> versus SO<sub>4</sub>-S, (2) H<sup>+</sup> versus SO<sub>4</sub>-S minus Ca, and (3) H<sup>+</sup> plus NH<sub>4</sub>-N versus SO<sub>4</sub>-S plus NO<sub>3</sub>-N, over periods of record, at 14 states in the US and 14 countries in Europe. Bold font indicates site at which inclusion of NO<sub>3</sub>-N and NH<sub>4</sub>-N improved correlation by more than 0.2

regionally steep declines in SO<sub>4</sub>-S in those US states most affected by acid precipitation after 2005, a pattern not observed in European countries. Despite declines, NO<sub>3</sub>-N in precipitation in 2007–2010 remained higher in most eastern European and some western European countries than anywhere in the US, perhaps because of differences in transportation patterns and population density.

There was no clear relationship between the concentration of SO<sub>4</sub>-S in precipitation and fossil fuel consumption per unit area across the countries examined for any period for which data were available. This could be due to many factors, including the type of fossil fuel used (coal vs. natural gas, for example), the quality of the fuel (high S vs. low S coal), or pollution control measures, all of which vary significantly among the countries used in this analysis. Before 1990, however, changes in SO<sub>4</sub>-S in precipitation over time were weakly related to changes in fossil fuel use among countries: countries with large increases in fossil fuel consumption experienced increased SO<sub>4</sub>-S in precipitation, while countries with smaller increases in fossil fuel use showed declining SO<sub>4</sub>-S in precipitation. After 1990, however, all countries showed declining SO<sub>4</sub>-S in precipitation, and SO<sub>4</sub>-S trends were not explained by trends in fossil energy use, suggesting that emission controls overwhelmed fossil fuel use effects on precipitation chemistry. For example, after 1990, SO<sub>4</sub>-S declined in Czechoslovakia, Germany, and Poland, where fossil fuel consumption also declined, but SO<sub>4</sub>-S declined even more steeply in The Netherlands, where fossil fuel use increased.

Although Hedin et al. (1994) noted synchronous patterns of base cation decline in three countries before 1991, we found that while most states and most countries in our expanded analysis showed at least some reduction in Ca levels from 1978 to 2010, these declines were not synchronous or universal. Starting in 1991 in the US, Ca (a proxy for both dust and industrial particulate emissions) did not decline even at sites most affected by regional industrial emissions despite continued widespread significant declines in SO<sub>4</sub>-S. Starting in 1991, in contrast, Ca declined in European countries (especially eastern Europe) where SO<sub>4</sub>-S and H<sup>+</sup> also continued to decline.

Hedin et al. (1994) and others have speculated that declines in particulate emissions were responsible for the slower decline of H<sup>+</sup> compared to SO<sub>4</sub>-S in precipitation in response to clean air legislation. Our results for the US are consistent with this interpretation, but it is not possible to determine if particulate control removed alkaline particles (e.g. CaO) that could neutralize acidity, or if particulate control reduced both cations and S-containing particulates that were not acidic, thus causing the lack of stoichiometry. In general, however, the stoichiometry between H<sup>+</sup> and SO<sub>4</sub>-S was remarkably good in the US, and adding in cations, NO<sub>3</sub>-N, or



**Fig. 7** a–c Countries with higher fossil energy use per unit area also had higher SO<sub>4</sub>-S in precipitation, although the relationship is strongest in 1990 and highly dependent on one high outlier

NH<sub>4</sub>-N, did not significantly improve correlations between the two. In many parts of Europe, however, declines in SO<sub>4</sub>-S were significantly greater than declines in H<sup>+</sup>, and accounting for declines in Ca (as a proxy for basic particles that could neutralize acidity) did not completely explain the lack of stoichiometry; rather, declining NH<sub>4</sub>-N was needed to improve trend analyses. In Europe, declining NH<sub>3</sub> emissions had the paradoxical effect of appearing to slow declines in precipitation H<sup>+</sup>, although the reduction in NH<sub>4</sub>-N deposition certainly has significant and positive ecological effects on its own.

Decades of acid rain research have documented negative effects in both terrestrial and aquatic ecosystems, and the legacy of acidic inputs is still debated. Some lakes are responding rapidly to declines in acidic

country (Netherlands), and becomes quite weak by 2000. (d), (e) Trends in SO<sub>4</sub>-S in precipitation as a function of trends in fossil energy use per unit area, 1970–1990 (d) and 1990–2005 (e)

inputs (e.g. Oulehle et al. 2008; Burton and Aherne 2012), while other studies of lakes show more mixed results (Stoddard et al. 1999), and modeling efforts suggest recovery of aquatic ecosystems might take decades (e.g. Sullivan et al. 2011). Terrestrial ecosystems have also been impacted, as acid deposition and the resulting soil base cation depletion have affected forest health and tree species composition (Federer et al. 1989; Gbondo-Tugbawa and Driscoll 2003, Joslin et al. 1992, Juice et al. 2006). Recovery of soil base saturation might take decades as well, even with improvements in tree health (Pannatier et al. 2005, Warby et al. 2009). Similarly, elevated NO<sub>3</sub>-N and NH<sub>4</sub>-N in deposition and N saturation (sensu Aber et al. 1998) are of significant concern globally, as excess N can have negative effects in both terrestrial and aquatic



ecosystems (Bowman et al. 2008, Emmett 2007, Greaver et al. 2012). Thus in both terrestrial and aquatic ecosystems with low buffering capacity, the legacy of the loss of base cations as well long term declines in alkaline inputs could delay recovery of ecosystem function.

This study provides the first comprehensive examination of trends in major constituents of precipitation chemistry from publically available monitoring records since 1978 in the US and Europe. Focusing on records from rural sites that were distant from urban and agricultural areas, we found no evidence of synchronous or continued declines in cation deposition. We argue that control of particulate emissions reduced both alkaline particles that neutralized acid precursors, and also reduced S-containing particulates, resulting in a pattern of reduced  $\text{SO}_4\text{-S}$  and cations. In Europe, significant declines in  $\text{NH}_3$  emissions contributed to a lack of stoichiometry between  $\text{SO}_4\text{-S}$  and  $\text{H}^+$  in precipitation. Continued efforts to control  $\text{SO}_2$ ,  $\text{NO}_x$ , and  $\text{NH}_3$  emissions should result in more sustained and stoichiometric decreases in  $\text{H}^+$ .

The future won't be the same as the past. The patterns of 1978–1990 (the era analyzed by Hedin et al. (1994), marked by renewable energy substitution) were different from those of 1991–2010 (the era marked by the collapse of eastern Europe economies and the advent of  $\text{NH}_4\text{-N}$  regulation), and the patterns of 2010–2030 will be yet different. Publically available long-term records from sites unaffected by local agricultural and urban signals are surprisingly rare, and continued maintenance of these records is essential to help understand the varying influences on precipitation acidity.

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## Appendix

See Table 9.

**Table 9** Annual concentrations of  $\text{H}^+$ ,  $\text{SO}_4\text{-S}$ , Ca,  $\text{NO}_3\text{-N}$ , and  $\text{NH}_4\text{-N}$  ( $\mu\text{eq/L}$ ) at the sites used in this study

Station	Year	$\text{H}^+$ (AZ99) ( $\mu\text{eq/L}$ )	$\text{SO}_4\text{-S}$ (AZ99) ( $\mu\text{eq/L}$ )	Ca (AZ99) ( $\mu\text{eq/L}$ )	$\text{NO}_3\text{-N}$ (AZ99) ( $\mu\text{eq/L}$ )	$\text{NH}_4\text{-N}$ (AZ99) ( $\mu\text{eq/L}$ )
AZ99	1981					
AZ99	1982	19.6	39.7	14.9	14.4	9.9
AZ99	1983	13.5	21.6	5.9	6.0	4.5
AZ99	1984	29.4	41.8	12.8	15.0	11.4
AZ99	1985	25.1	34.6	7.5	12.1	7.9
AZ99	1986	20.3	32.4	6.6	10.8	6.9
AZ99	1987	18.6	33.1	11.3	13.5	8.3
AZ99	1988	18.3	26.0	6.1	11.8	5.4
AZ99	1989	3.0	23.0	15.2	14.0	11.6
AZ99	1990	9.2	20.7	8.8	14.7	14.2
AZ99	1991	10.7	17.7	5.8	11.2	7.9
AZ99	1992	8.6	21.7	8.1	12.3	10.4
AZ99	1993	7.6	20.4	12.7	9.9	9.1
AZ99	1994	12.6	18.3	8.3	14.0	11.5
AZ99	1995	10.4	15.6	16.6	11.2	9.8
AZ99	1996	12.2	16.8	9.3	12.4	8.4
AZ99	1997	14.8	26.4	11.5	15.9	13.4
AZ99	1998	13.2	22.5	10.3	14.6	11.6
AZ99	1999	13.6	19.8	11.9	22.3	16.4
AZ99	2000	8.7	11.2	8.4	12.3	7.7
AZ99	2001	11.7	19.3	9.9	18.7	16.1
AZ99	2002	5.9	18.4	10.7	20.3	22.2
AZ99	2003	6.3	20.0	13.1	20.9	23.8
AZ99	2004	7.2	14.6	7.8	16.4	17.4
AZ99	2005	8.5	14.4	7.8	13.7	13.4
AZ99	2006	9.5	16.2	12.3	20.3	17.5
AZ99	2007	5.8	14.0	11.1	14.4	16.6
AZ99	2008	7.4	14.2	9.9	15.0	13.4
AZ99	2009	8.8	17.0	22.8	17.3	18.6
AZ99	2010	4.8	9.8	7.5	13.6	14.3
Station	Year	$\text{H}^+$ (CA99) ( $\mu\text{eq/L}$ )	$\text{SO}_4\text{-S}$ (CA99) ( $\mu\text{eq/L}$ )	Ca (CA99) ( $\mu\text{eq/L}$ )	$\text{NO}_3\text{-N}$ (CA99) ( $\mu\text{eq/L}$ )	$\text{NH}_4\text{-N}$ (CA99) ( $\mu\text{eq/L}$ )
CA99	1981					
CA99	1982	4.1	4.3	1.5	3.2	3.1
CA99	1983	3.4	5.6	2.1	5.0	4.8
CA99	1984	3.3	9.0	4.4	7.4	6.0
CA99	1985	4.5	6.2	2.3	8.4	7.1
CA99	1986	5.3	11.5	4.1	15.9	13.1
CA99	1987	5.0	5.5	2.3	8.0	6.4
CA99	1988	3.8	5.9	3.5	7.0	3.7
CA99	1989	3.5	9.1	3.1	16.5	18.6
CA99	1990	3.4	6.9	2.1	12.6	14.7
CA99	1991	4.0	5.2	2.4	6.8	4.7
CA99	1992	3.4	3.5	1.1	6.1	5.8

**Table 9** continued

Station	Year	H <sup>+</sup> (CA99) (μeq/L)	SO <sub>4</sub> -S (CA99) (μeq/L)	Ca (CA99) (μeq/L)	NO <sub>3</sub> -N (CA99) (μeq/L)	NH <sub>4</sub> -N (CA99) (μeq/L)
CA99	1993	2.7	7.3	2.9	12.3	15.1
CA99	1994	5.8	4.5	1.3	7.8	6.9
CA99	1995	4.0	2.7	1.0	4.0	4.7
CA99	1996	3.4	2.3	1.3	2.8	2.6
CA99	1997	4.6	2.8	1.2	5.6	4.3
CA99	1998	4.4	4.6	1.4	9.6	10.7
CA99	1999	3.1	3.6	2.0	7.5	9.1
CA99	2000	3.5	3.5	1.3	5.1	5.9
CA99	2001	3.7	4.2	2.3	6.4	7.6
CA99	2002	3.4	4.1	2.1	6.1	8.1
CA99	2003	2.7	4.9	2.4	8.5	13.0
CA99	2004	3.1	3.9	1.5	5.2	7.7
CA99	2005	3.8	3.5	1.3	4.5	5.3
CA99	2006	2.9	4.4	2.2	6.1	9.4
CA99	2007	2.7	3.3	1.4	4.9	9.2
CA99	2008	2.4	4.4	5.3	5.0	4.3
CA99	2009	3.1	3.7	1.7	3.3	6.1
CA99	2010	3.0	3.4	1.4	4.4	7.8
Station	Year	H <sup>+</sup> (CO99) (μeq/L)	SO <sub>4</sub> -S (CO99) (μeq/L)	Ca (CO99) (μeq/L)	NO <sub>3</sub> -N (CO99) (μeq/L)	NH <sub>4</sub> -N (CO99) (μeq/L)
CO99	1981	18.7	44.6	34.6	21.1	8.3
CO99	1982	20.2	29.8	16.2	14.4	7.4
CO99	1983	13.2	20.1	14.0	11.3	4.9
CO99	1984	17.7	31.4	44.3	19.9	9.3
CO99	1985	12.2	22.3	18.4	11.6	4.1
CO99	1986	12.9	19.8	15.5	11.6	4.7
CO99	1987	16.0	22.5	11.5	15.2	7.3
CO99	1988	15.1	23.7	28.8	16.8	4.1
CO99	1989	10.9	24.9	25.4	20.7	11.6
CO99	1990	13.6	27.3	38.8	19.4	9.8
CO99	1991	13.6	21.1	22.7	14.3	5.4
CO99	1992	11.4	18.7	9.6	14.1	9.5
CO99	1993	9.5	16.0	9.9	11.9	6.2
CO99	1994	16.0	21.2	13.7	17.8	8.3
CO99	1995	12.2	18.1	13.3	14.0	9.2
CO99	1996	9.4	20.6	35.2	19.5	12.8
CO99	1997	13.7	16.7	12.1	15.4	6.8
CO99	1998	15.1	18.6	17.1	14.7	7.4
CO99	1999	18.7	20.9	15.5	21.9	8.8
CO99	2000	13.0	18.4	18.4	23.1	9.8
CO99	2001	13.5	18.0	17.2	20.4	9.4
CO99	2002	3.5	15.8	30.0	17.0	15.7
CO99	2003	5.9	12.1	22.9	13.6	9.7
CO99	2004	9.1	12.7	15.9	15.8	9.9
CO99	2005	11.7	13.9	10.7	14.9	9.1
CO99	2006	7.8	13.2	18.8	19.1	11.6

**Table 9** continued

Station	Year	H <sup>+</sup> (CO99) (μeq/L)	SO <sub>4</sub> -S (CO99) (μeq/L)	Ca (CO99) (μeq/L)	NO <sub>3</sub> -N (CO99) (μeq/L)	NH <sub>4</sub> -N (CO99) (μeq/L)
CO99	2007	11.0	14.4	18.2	18.6	10.8
CO99	2008	6.3	11.0	22.7	14.6	7.9
CO99	2009	6.3	23.0		17.9	11.8
CO99	2010	7.6	9.9	17.5	13.7	9.5
Station	Year	H <sup>+</sup> (GA41) (μeq/L)	SO <sub>4</sub> -S (GA41) (μeq/L)	Ca (GA41) (μeq/L)	NO <sub>3</sub> -N (GA41) (μeq/L)	NH <sub>4</sub> -N (GA41) (μeq/L)
GA41	1979	23.6	35.4	4.0	11.5	16.5
GA41	1980	32.6	41.0	5.2	14.8	7.0
GA41	1981	31.0	43.6	7.5	14.2	10.9
GA41	1982	26.1	36.1	5.6	11.4	8.8
GA41	1983	15.4	25.3	5.8	10.4	9.7
GA41	1984	27.9	33.3	7.2	12.8	8.8
GA41	1985	33.7	36.1	3.9	14.7	8.6
GA41	1986	36.8	42.3	4.2	15.1	9.0
GA41	1987	21.6	28.0	3.5	10.3	7.1
GA41	1988	30.3	33.6	3.6	11.6	5.0
GA41	1989	18.5	23.1	3.1	10.1	8.4
GA41	1990	25.3	31.6	2.9	11.5	10.4
GA41	1991	29.0	31.7	3.4	13.8	9.4
GA41	1992	16.2	21.9	2.4	9.2	10.0
GA41	1993	29.6	31.2	2.7	13.6	9.0
GA41	1994	19.9	21.3	2.4	9.6	8.0
GA41	1995	22.4	24.5	3.4	12.8	11.9
GA41	1996	23.8	25.2	3.4	10.6	8.2
GA41	1997	21.6	21.5	1.6	10.1	8.3
GA41	1998	26.4	30.6	4.9	14.7	14.1
GA41	1999	23.9	29.2	4.1	14.0	13.7
GA41	2000	31.8	31.3	3.4	15.0	9.1
GA41	2001	17.7	20.7	3.0	10.4	8.2
GA41	2002	18.7	24.4	3.0	11.6	14.4
GA41	2003	14.1	23.1	4.1	11.0	14.2
GA41	2004	16.6	22.7	3.2	9.9	15.9
GA41	2005	15.3	24.3	3.6	12.0	16.6
GA41	2006	16.9	29.3	4.5	11.0	19.1
GA41	2007	19.4	23.6	3.1	9.9	15.1
GA41	2008	14.1	18.9	3.6	8.5	10.0
GA41	2009	7.8	10.9	2.2	5.0	8.1
GA41	2010	13.1	16.2	2.5	8.7	11.9
Station	Year	H <sup>+</sup> (MI26) (μeq/L)	SO <sub>4</sub> -S (MI26) (μeq/L)	Ca (MI26) (μeq/L)	NO <sub>3</sub> -N (MI26) (μeq/L)	NH <sub>4</sub> -N (MI26) (μeq/L)
MI26	1979	56.4	77.4	13.5	34.5	24.4
MI26	1980	49.0	76.2	15.9	36.8	27.5
MI26	1981	46.6	68.2	15.1	29.4	24.4
MI26	1982	48.6	61.4	12.3	30.8	21.3
MI26	1983	49.2	58.4	12.3	34.0	23.7
MI26	1984	41.5	53.2	12.0	28.0	20.7

**Table 9** continued

Station	Year	H <sup>+</sup> (MI26) (μeq/L)	SO <sub>4</sub> -S (MI26) (μeq/L)	Ca (MI26) (μeq/L)	NO <sub>3</sub> -N (MI26) (μeq/L)	NH <sub>4</sub> -N (MI26) (μeq/L)
MI26	1985	47.6	59.1	9.5	28.2	22.1
MI26	1986	42.5	57.1	9.1	27.3	23.9
MI26	1987	52.4	66.4	11.1	35.4	25.9
MI26	1988	36.4	54.8	12.2	29.1	22.0
MI26	1989	43.5	64.1	14.3	32.9	31.5
MI26	1990	42.2	53.3	10.4	27.9	24.1
MI26	1991	34.2	44.3	8.8	24.4	21.1
MI26	1992	34.4	44.2	8.9	26.9	20.0
MI26	1993	40.2	47.5	8.5	29.9	22.3
MI26	1994	40.8	45.2	7.4	26.3	21.8
MI26	1995	33.7	42.4	10.1	30.1	26.7
MI26	1996	36.6	46.9	10.6	30.4	27.1
MI26	1997	29.2	41.0	10.0	30.0	27.6
MI26	1998	35.2	47.8	10.8	32.9	29.2
MI26	1999	33.6	42.5	10.0	30.4	24.3
MI26	2000	23.1	35.4	9.5	26.1	23.0
MI26	2001	24.4	35.9	9.2	25.7	24.4
MI26	2002	19.1	33.8	10.5	25.3	24.6
MI26	2003	18.4	38.0	13.1	28.3	33.8
MI26	2004	21.6	37.4	10.5	25.1	28.6
MI26	2005	25.5	39.5	11.4	26.0	27.8
MI26	2006	18.5	28.4	8.6	21.1	23.5
MI26	2007	17.7	33.0	11.0	22.0	27.6
MI26	2008	15.1	24.2	6.8	15.8	18.0
MI26	2009	10.6	22.3	7.7	15.5	21.5
MI26	2010	11.5	22.7	7.7	17.4	23.8
Station	Year	H <sup>+</sup> (MN16) (μeq/L)	SO <sub>4</sub> -S (MN16) (μeq/L)	Ca (MN16) (μeq/L)	NO <sub>3</sub> -N (MN16) (μeq/L)	NH <sub>4</sub> -N (CO99) (μeq/L)
MN16	1978	7.8	24.4	13.1	16.8	13.8
MN16	1979	13.0	41.1	15.5	24.7	25.4
MN16	1980	8.6	27.8	11.6	20.7	20.0
MN16	1981	8.5	27.5	11.7	17.6	18.7
MN16	1982	10.2	26.6	10.4	15.4	17.2
MN16	1983	13.0	28.2	11.2	18.9	21.4
MN16	1984	9.5	27.5	12.5	16.7	20.7
MN16	1985	7.2	21.4	10.6	13.5	14.2
MN16	1986	9.3	24.1	9.9	16.5	18.6
MN16	1987	10.7	23.0	7.6	16.5	18.8
MN16	1988	7.5	18.6	9.7	15.7	11.5
MN16	1989	7.3	24.7	10.4	18.7	26.7
MN16	1990	8.8	20.4	9.7	18.3	21.2
MN16	1991	9.1	20.9	10.1	16.2	16.3
MN16	1992	9.7	20.2	7.4	15.7	18.6
MN16	1993	8.2	18.2	7.0	15.9	16.2
MN16	1994	5.9	16.6	10.7	17.7	22.3

**Table 9** continued

Station	Year	H <sup>+</sup> (MN16) (μeq/L)	SO <sub>4</sub> -S (MN16) (μeq/L)	Ca (MN16) (μeq/L)	NO <sub>3</sub> -N (MN16) (μeq/L)	NH <sub>4</sub> -N (CO99) (μeq/L)
MN16	1995	10.1	13.5	5.5	13.8	15.0
MN16	1996	10.3	14.8	8.3	16.4	13.4
MN16	1997	10.0	12.5	7.5	14.7	12.8
MN16	1998	9.1	17.6	7.7	16.1	21.5
MN16	1999	6.7	17.8	10.5	17.5	22.3
MN16	2000	6.8	16.4	9.5	17.8	20.9
MN16	2001	4.9	12.2	9.6	13.3	14.9
MN16	2002	3.5	16.9	10.5	17.4	26.1
MN16	2003	4.5	15.1	9.8	15.9	23.2
MN16	2004	5.3	16.0	8.6	15.4	23.6
MN16	2005	5.9	16.9	9.2	16.0	22.2
MN16	2006	4.1	17.4	11.9	17.2	25.3
MN16	2007	5.3	16.0	10.7	14.8	26.2
MN16	2008	3.6	15.6	11.6	14.3	24.5
MN16	2009	3.8	12.3	8.9	11.4	19.0
MN16	2010	3.6	9.7	7.9	10.2	16.7
Station	Year	H <sup>+</sup> (NC25) (μeq/L)	SO <sub>4</sub> -S (NC25) (μeq/L)	Ca (NC25) (μeq/L)	NO <sub>3</sub> -N (NC25) (μeq/L)	NH <sub>4</sub> -N (NC25) (μeq/L)
NC25	1978	23.9	25.1	2.5	7.9	2.4
NC25	1979	22.0	32.7	3.5	10.1	7.0
NC25	1980	33.1	36.2	3.6	13.5	6.0
NC25	1981	30.5	37.1	5.5	13.6	9.8
NC25	1982	21.3	26.1	3.1	9.5	6.3
NC25	1983	20.0	25.4	4.0	10.2	9.2
NC25	1984	22.2	30.5	7.9	12.3	11.6
NC25	1985	36.3	37.3	2.7	12.3	7.2
NC25	1986	27.5	31.5	3.6	13.2	7.2
NC25	1987	31.4	32.3	2.5	12.3	7.3
NC25	1988	33.6	36.2	3.2	13.5	5.4
NC25	1989	21.9	24.2	2.5	10.5	8.7
NC25	1990	21.3	23.8	2.1	9.9	8.7
NC25	1991	26.3	28.5	3.8	12.2	7.1
NC25	1992	20.4	21.7	1.2	8.7	5.9
NC25	1993	22.2	23.3	2.0	10.7	6.9
NC25	1994	21.0	21.5	2.7	9.9	7.5
NC25	1995	21.3	21.1	2.2	10.7	8.4
NC25	1996	23.4	22.3	3.0	11.7	7.9
NC25	1997	23.2	21.8	1.9	10.8	6.8
NC25	1998	18.2	18.1	3.1	9.8	6.4
NC25	1999	22.0	23.7	4.0	12.5	9.9
NC25	2000	23.0	23.4	3.1	12.7	8.4
NC25	2001	23.3	23.2	2.1	11.0	7.2
NC25	2002	15.9	17.1	1.9	9.1	7.1
NC25	2003	18.3	19.4	2.5	9.8	8.2
NC25	2004	18.5	19.2	2.4	9.2	8.0

Table 9 continued

Station	Year	H <sup>+</sup> (NC25) (μeq/L)	SO <sub>4</sub> -S (NC25) (μeq/L)	Ca (NC25) (μeq/L)	NO <sub>3</sub> -N (NC25) (μeq/L)	NH <sub>4</sub> -N (NC25) (μeq/L)
NC25	2005	19.1	20.7	2.7	9.7	9.0
NC25	2006	23.0	26.8	3.6	10.7	9.8
NC25	2007	26.2	31.6	3.6	11.5	14.3
NC25	2008	13.6	17.2	4.5	8.4	7.6
NC25	2009	9.6	10.8	2.3	6.2	6.3
NC25	2010	11.9	12.2	2.9	8.3	7.0

Station	Year	H <sup>+</sup> (NH02) (μeq/L)	SO <sub>4</sub> -S (NH02) (μeq/L)	Ca (NH02) (μeq/L)	NO <sub>3</sub> -N (NH02) (μeq/L)	NH <sub>4</sub> -N (NH02) (μeq/L)
NH02	1978	63.1	47.6	5.8	30.8	6.9
NH02	1979	38.2	43.0	5.1	22.2	5.7
NH02	1980	54.7	51.3	5.4	29.7	9.0
NH02	1981	46.2	48.5	6.4	21.2	11.4
NH02	1982	45.9	41.5	3.8	25.0	9.8
NH02	1983	36.8	34.3	3.3	19.1	9.3
NH02	1984	38.8	34.5	3.9	20.7	9.2
NH02	1985	45.8	37.5	3.4	24.6	9.0
NH02	1986	44.3	39.7	2.0	19.3	7.7
NH02	1987	37.2	33.9	2.4	18.8	8.4
NH02	1988	48.4	45.3	4.4	25.3	8.3
NH02	1989	42.3	38.9	3.3	24.1	13.5
NH02	1990	36.7	32.5	2.1	18.7	8.1
NH02	1991	43.8	37.5	2.3	21.6	8.8
NH02	1992	41.2	36.2	2.1	22.2	9.5
NH02	1993	36.0	31.4	2.0	22.0	7.9
NH02	1994	42.1	33.1	2.6	24.0	11.2
NH02	1995	38.7	29.7	2.3	22.7	12.2
NH02	1996	33.1	27.0	2.4	18.9	9.1
NH02	1997	40.4	32.3	2.3	23.8	11.0
NH02	1998	35.5	28.5	3.0	20.5	9.5
NH02	1999	29.0	24.8	2.9	17.3	7.8
NH02	2000	31.8	27.1	2.9	19.5	9.9
NH02	2001	30.1	23.6	2.8	20.3	8.2
NH02	2002	25.5	23.9	2.8	17.8	10.5
NH02	2003	25.0	21.9	2.4	14.1	6.9
NH02	2004	30.0	24.1	2.5	16.8	8.5
NH02	2005	21.8	20.4	1.9	11.5	7.9
NH02	2006	20.2	17.5	2.3	11.2	6.5
NH02	2007	24.2	26.0	2.7	13.5	12.8
NH02	2008	20.0	16.7	2.2	11.9	6.8
NH02	2009	14.8	12.7	2.0	10.0	6.4
NH02	2010	12.5	11.9	2.6	8.6	6.9

Station	Year	H <sup>+</sup> (NY20) (μeq/L)	SO <sub>4</sub> -S (NY20) (μeq/L)	Ca (NY20) (μeq/L)	NO <sub>3</sub> -N (NY20) (μeq/L)	NH <sub>4</sub> -N (NY20) (μeq/L)
NY20	1978	47.3	26.1	3.5	22.9	2.7
NY20	1979	38.5	40.5	5.0	22.7	7.8
NY20	1980	59.6	58.0	6.6	30.9	16.0

Table 9 continued

Station	Year	H <sup>+</sup> (NY20) (μeq/L)	SO <sub>4</sub> -S (NY20) (μeq/L)	Ca (NY20) (μeq/L)	NO <sub>3</sub> -N (NY20) (μeq/L)	NH <sub>4</sub> -N (NY20) (μeq/L)
NY20	1981	46.0	51.5	8.3	25.9	14.7
NY20	1982	41.9	47.6	5.2	21.7	14.2
NY20	1983	36.8	39.5	5.3	20.2	12.3
NY20	1984	37.5	36.8	5.2	20.9	10.3
NY20	1985	42.4	39.7	5.0	23.8	9.9
NY20	1986	44.6	43.3	3.1	21.8	11.0
NY20	1987	44.1	40.6	4.2	24.8	12.3
NY20	1988	53.1	50.3	5.1	27.4	11.4
NY20	1989	36.3	36.0	5.2	23.1	12.9
NY20	1990	39.1	35.3	3.6	21.6	10.2
NY20	1991	38.1	34.9	3.8	21.9	10.1
NY20	1992	30.8	28.2	2.8	18.1	8.4
NY20	1993	41.3	35.1	3.1	24.0	10.2
NY20	1994	45.0	40.4	3.2	22.8	13.5
NY20	1995	36.0	30.8	3.2	20.8	12.8
NY20	1996	31.1	26.4	4.2	20.0	10.2
NY20	1997	36.6	28.8	2.9	22.6	9.3
NY20	1998	36.4	30.8	3.5	21.2	10.1
NY20	1999	27.8	22.2	3.0	18.4	7.5
NY20	2000	29.0	24.9	4.1	20.4	9.9
NY20	2001	32.0	27.2	3.1	20.8	10.6
NY20	2002	27.2	26.3	4.1	21.4	12.3
NY20	2003	24.0	23.1	3.8	16.9	11.7
NY20	2004	30.0	25.9	3.5	18.2	10.4
NY20	2005	21.8	19.1	2.4	13.4	7.9
NY20	2006	20.4	19.7	3.3	12.0	7.7
NY20	2007	24.4	24.8	3.7	15.0	12.0
NY20	2008	22.5	22.7	3.4	12.5	9.6
NY20	2009	15.7	14.8	3.2	11.7	8.8
NY20	2010	10.3	10.7	2.7	8.4	8.7

Station	Year	H <sup>+</sup> (OH71) (μeq/L)	SO <sub>4</sub> -S (OH71) (μeq/L)	Ca (OH71) (μeq/L)	NO <sub>3</sub> -N (OH71) (μeq/L)	NH <sub>4</sub> -N (OH71) (μeq/L)
OH71	1978	54.5	76.8	12.1	25.1	18.0
OH71	1979	54.6	77.4	11.6	27.4	17.8
OH71	1980	67.9	74.8	10.5	29.7	18.2
OH71	1981	59.7	71.9	12.1	29.5	23.5
OH71	1982	57.0	68.7	9.9	29.4	23.0
OH71	1983	56.0	63.4	10.0	27.9	20.4
OH71	1984	60.8	69.6	11.0	34.3	27.5
OH71	1985	61.2	66.5	7.6	28.1	20.0
OH71	1986	59.0	73.7	9.6	32.2	24.3
OH71	1987	60.7	75.3	10.5	33.5	27.6
OH71	1988	64.9	75.3	10.7	32.9	16.1
OH71	1989	58.1	68.4	8.3	31.4	25.5
OH71	1990	56.4	60.3	5.5	23.9	18.3

**Table 9** continued

Station	Year	H <sup>+</sup> (OH71) (μeq/L)	SO <sub>4</sub> -S (OH71) (μeq/L)	Ca (OH71) (μeq/L)	NO <sub>3</sub> -N (OH71) (μeq/L)	NH <sub>4</sub> -N (OH71) (μeq/L)
OH71	1991	57.0	68.6	11.4	33.1	27.1
OH71	1992	58.2	66.3	7.9	28.1	23.1
OH71	1993	44.3	49.7	7.0	24.5	18.2
OH71	1994	61.7	70.1	9.0	33.5	26.4
OH71	1995	48.0	51.7	8.0	27.5	21.5
OH71	1996	44.4	47.8	8.4	28.0	20.5
OH71	1997	52.7	54.8	6.9	29.7	20.6
OH71	1998	41.1	45.9	8.8	27.2	20.8
OH71	1999	43.9	48.9	10.1	30.1	20.8
OH71	2000	41.2	47.2	7.7	25.4	19.4
OH71	2001	35.9	51.6	11.1	27.7	25.4
OH71	2002	34.4	46.8	9.8	26.4	22.1
OH71	2003	31.3	41.4	8.6	22.8	21.8
OH71	2004	32.7	40.5	7.1	19.6	18.7
OH71	2005	33.3	46.9	9.3	24.0	25.1
OH71	2006	29.9	41.0	9.1	22.3	23.3
OH71	2007	29.4	37.3	6.8	16.7	19.2
OH71	2008	24.3	35.7	8.7	18.8	21.8
OH71	2009	15.6	27.5	7.7	14.3	19.6
OH71	2010	11.2	22.4	5.9	12.9	20.9
Station	Year	H <sup>+</sup> (OR10) (μeq/L)	SO <sub>4</sub> -S (OR10) (μeq/L)	Ca (OR10) (μeq/L)	NO <sub>3</sub> -N (OR10) (μeq/L)	NH <sub>4</sub> -N (OR10) (μeq/L)
OR10	1980	3.2	5.3	2.0	1.8	1.0
OR10	1981	3.7	6.6	2.4	2.0	0.6
OR10	1982	4.1	6.1	1.5	2.3	1.0
OR10	1983	3.8	6.8	2.0	2.1	1.4
OR10	1984	3.7	6.4	1.8	2.1	1.7
OR10	1985	4.9	4.9	1.9	2.0	0.7
OR10	1986	4.2	3.8	1.4	1.4	1.1
OR10	1987	4.5	4.3	1.9	2.4	1.2
OR10	1988	4.4	3.9	1.6	1.3	0.8
OR10	1989	3.8	3.7	1.2	2.2	1.2
OR10	1990	4.4	4.0	1.2	2.3	1.5
OR10	1991	4.4	3.9	1.1	2.7	1.1
OR10	1992	3.9	3.5	1.0	2.3	1.2
OR10	1993	4.3	4.1	1.3	2.9	1.4
OR10	1994	4.9	3.4	1.1	2.1	1.7
OR10	1995	4.8	2.8	0.8	2.1	1.2
OR10	1996	4.5	3.5	1.4	1.7	1.1
OR10	1997	5.3	3.8	0.9	2.5	1.1
OR10	1998	4.7	2.7	0.9	1.8	0.7
OR10	1999	4.2	3.2	1.2	1.7	1.2
OR10	2000	5.2	3.2	1.0	2.3	0.7
OR10	2001	4.9	3.5	1.6	2.3	0.9

**Table 9** continued

Station	Year	H <sup>+</sup> (OR10) (μeq/L)	SO <sub>4</sub> -S (OR10) (μeq/L)	Ca (OR10) (μeq/L)	NO <sub>3</sub> -N (OR10) (μeq/L)	NH <sub>4</sub> -N (OR10) (μeq/L)
OR10	2002	4.7	3.1	1.2	2.1	0.8
OR10	2003	4.6	2.9	0.9	1.9	1.1
OR10	2004	5.1	3.3	1.1	2.2	0.8
OR10	2005	4.7	3.6	1.2	2.3	1.1
OR10	2006	4.3	3.4	1.8	1.7	0.8
OR10	2007	4.7	3.4	1.3	1.7	0.9
OR10	2008	4.6	3.7	1.2	1.5	1.1
OR10	2009	4.3	4.4	4.0	1.9	1.2
OR10	2010	4.6	2.9	1.3	1.7	0.9
Station	Year	H <sup>+</sup> (PA29) (μeq/L)	SO <sub>4</sub> -S (PA29) (μeq/L)	Ca (PA29) (μeq/L)	NO <sub>3</sub> -N (PA29) (μeq/L)	NH <sub>4</sub> -N (PA29) (μeq/L)
PA29	1978	106.4	75.9	6.6	33.1	14.0
PA29	1979	72.4	81.4	7.4	32.3	15.1
PA29	1980	72.8	72.1	8.3	32.0	14.1
PA29	1981	60.8	57.9	7.9	33.9	15.6
PA29	1982	65.5	66.2	6.9	30.7	14.5
PA29	1983	63.5	63.1	7.2	24.0	14.1
PA29	1984	65.2	64.0	5.8	29.3	17.2
PA29	1985	63.1	59.1	5.4	28.6	13.9
PA29	1986	76.9	73.5	5.8	32.6	15.6
PA29	1987	70.6	68.5	4.9	28.7	15.5
PA29	1988	66.5	67.6	8.8	35.8	15.7
PA29	1989	63.7	60.3	4.4	28.1	15.1
PA29	1990	61.4	57.4	4.6	26.7	13.9
PA29	1991	63.1	61.0	6.5	35.1	18.7
PA29	1992	53.5	53.7	5.2	24.4	13.3
PA29	1993	51.5	46.3	4.1	27.2	11.0
PA29	1994	61.5	56.4	4.8	27.7	14.9
PA29	1995	53.7	46.9	5.6	30.9	16.6
PA29	1996	47.3	44.1	5.0	24.5	14.6
PA29	1997	50.9	44.6	4.8	28.1	13.8
PA29	1998	55.2	49.6	4.2	26.0	13.2
PA29	1999	45.0	40.9	6.2	25.9	11.4
PA29	2000	55.2	55.1	6.9	30.5	18.0
PA29	2001	44.6	44.4	6.3	25.8	14.4
PA29	2002	39.0	41.2	4.9	23.9	15.3
PA29	2003	51.6	53.1	5.6	24.9	16.5
PA29	2004	37.2	35.8	3.9	16.5	10.8
PA29	2005	39.2	41.7	4.1	17.3	13.3
PA29	2006	38.2	39.7	4.5	16.8	13.2
PA29	2007	40.6	43.5	5.1	20.6	17.4
PA29	2008	35.5	36.0	5.2	18.2	13.3
PA29	2009	26.4	30.4	4.2	13.5	11.8
PA29	2010	20.2	21.8	3.4	11.2	9.5

**Table 9** continued

Station	Year	H <sup>+</sup> (WA14) (μeq/L)	SO <sub>4</sub> -S (WA14) (μeq/L)	Ca (WA14) (μeq/L)	NO <sub>3</sub> -N (WA14) (μeq/L)	NH <sub>4</sub> -N (WA14) (μeq/L)
WA14	1980	3.9	7.0	1.6	1.5	0.6
WA14	1981	4.0	8.1	3.5	1.5	0.7
WA14	1982	3.9	7.5	2.2	1.1	0.9
WA14	1983	3.5	6.0	2.2	1.2	0.8
WA14	1984	3.4	7.4	2.5	1.3	1.3
WA14	1985	4.3	6.6	2.2	0.7	0.6
WA14	1986	4.0	5.6	1.7	0.7	0.6
WA14	1987	4.4	6.3	2.0	1.6	0.7
WA14	1988	4.4	5.9	1.9	0.9	0.6
WA14	1989	3.5	4.4	1.0	1.3	1.2
WA14	1990	4.1	5.7	1.7	1.6	2.3
WA14	1991	4.1	4.5	1.5	1.5	0.6
WA14	1992	3.6	5.0	1.8	1.6	0.8
WA14	1993	4.0	5.2	1.5	1.8	1.4
WA14	1994	5.0	5.0	1.4	1.5	0.9
WA14	1995	5.1	4.6	1.1	1.8	1.2
WA14	1996	4.9	5.0	1.3	1.5	1.1
WA14	1997	5.1	5.3	1.5	1.8	0.7
WA14	1998	4.5	4.3	1.4	1.3	0.6
WA14	1999	4.5	5.7	2.0	1.2	0.9
WA14	2000	5.7	5.2	1.4	2.2	0.6
WA14	2001	4.6	5.5	1.9	1.3	0.7
WA14	2002	4.2	5.0	1.7	1.5	0.7
WA14	2003	4.1	4.5	1.6	1.3	0.8
WA14	2004	4.6	4.5	1.6	1.6	0.6
WA14	2005	4.7	5.1	1.8	1.6	0.6
WA14	2006	4.8	5.8	2.7	1.9	0.7
WA14	2007	5.3	5.3	1.6	1.8	0.7
WA14	2008	4.6	6.6	2.4	1.5	0.8
WA14	2009	4.2	5.2	2.1	1.1	0.4
WA14	2010	4.2	5.4	2.4	1.5	0.6
Station	Year	H <sup>+</sup> (WV18) (μeq/L)	SO <sub>4</sub> -S (WV18) (μeq/L)	Ca (WV18) (μeq/L)	NO <sub>3</sub> -N (WV18) (μeq/L)	NH <sub>4</sub> -N (WV18) (μeq/L)
WV18	1978	55.0	62.4	7.5	21.3	10.0
WV18	1979	55.0	69.8	11.5	28.2	13.4
WV18	1980	68.5	74.2	14.4	32.8	13.4
WV18	1981	66.7	73.7	14.4	30.4	15.8
WV18	1982	48.6	55.0	7.7	20.9	11.0
WV18	1983	50.9	52.5	8.0	22.5	11.4
WV18	1984	48.6	51.2	7.5	22.1	10.6
WV18	1985	64.4	66.2	8.8	26.2	12.5
WV18	1986	75.7	82.5	11.3	33.2	16.0
WV18	1987	61.0	63.7	8.5	29.3	15.4
WV18	1988	56.6	61.5	9.1	26.0	9.3
WV18	1989	59.0	58.2	5.9	25.1	13.7
WV18	1990	51.9	51.8	5.9	23.0	11.9

**Table 9** continued

Station	Year	H <sup>+</sup> (NC25) (μeq/L)	SO <sub>4</sub> -S (NC25) (μeq/L)	Ca (NC25) (μeq/L)	NO <sub>3</sub> -N (NC25) (μeq/L)	NH <sub>4</sub> -N (NC25) (μeq/L)
WV18	1991	57.9	58.2	7.5	26.2	11.1
WV18	1992	54.1	55.4	8.1	28.6	12.6
WV18	1993	54.6	54.2	7.5	26.6	11.4
WV18	1994	55.1	53.2	5.4	23.3	13.0
WV18	1995	43.9	40.9	6.6	26.9	16.5
WV18	1996	40.6	38.6	5.8	21.7	11.6
WV18	1997	41.8	36.7	4.6	22.4	9.7
WV18	1998	50.5	48.4	6.2	25.1	12.5
WV18	1999	37.2	38.7	6.8	21.2	10.9
WV18	2000	35.3	32.6	5.8	21.2	9.8
WV18	2001	40.6	40.2	5.1	21.6	12.8
WV18	2002	32.6	35.4	4.4	17.6	11.8
WV18	2003	33.0	33.2	4.7	17.4	11.1
WV18	2004	36.4	36.5	4.6	15.5	9.9
WV18	2005	31.4	33.5	5.5	17.2	11.9
WV18	2006	37.5	41.2	6.5	16.6	13.2
WV18	2007	34.4	36.7	5.7	15.8	12.6
WV18	2008	24.2	29.7	6.0	14.1	12.5
WV18	2009	15.2	17.3	4.3	9.7	7.4
WV18	2010	20.9	23.1	6.8	16.0	10.9

Data are from NADP and the EMEP (Collaborative program for monitoring and evaluation of the long-range transmission of air pollutants in Europe) project (<http://www.nilu.no/projects/ccc/emep/data.html>)

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