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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 SO_2 and 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 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 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 $\text{SO}_4\text{-S}$, H^+ , $\text{NH}_4\text{-N}$, Ca, and $\text{NO}_3\text{-N}$, (2) assess stoichiometry between 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 vs. gaseous emission, along with trends in NH_3 emissions, would be the two most significant factors affecting the stoichiometry between $\text{SO}_4\text{-S}$ and H^+ .

Relationships among 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, 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 NH_3 , which neutralizes acidity upon conversion to NH_4^+ , is generally significantly higher in Europe than in the US. Trends in $\text{SO}_4\text{-S}$ and 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 H^+ may be explained in part by emission controls, which varied over time and among regions. Control of gaseous SO_2 emissions results in a stoichiometric relationship between $\text{SO}_4\text{-S}$ and H^+ , consistent with trends in the US and many western European countries, especially after 1991. In contrast, control of particulate emissions reduces alkaline particles that neutralize acid precursors as well as S-containing particulates, reducing $\text{SO}_4\text{-S}$ and Ca more steeply than H^+ , consistent with trends in the northeastern US and Europe before 1990. However, in many European countries, declining NH_3 emissions contributed to the lack of stoichiometry between $\text{SO}_4\text{-S}$ and H^+ .

Recent reductions in NO_x emissions have also contributed to declines in H^+ in precipitation. Future changes in precipitation acidity are likely to depend on multiple factors including trends in NO_x and NH_3 emission controls, naturally occurring dust, and fossil fuel use, with significant implications for the health of both terrestrial and aquatic ecosystems.

Introduction

60 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 SO_2 and NO_x resulting in the formation
and deposition of sulfuric and nitric acids. Acid rain has had significant effects on both
65 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
70 reduce 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-
75 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, SO_2 emissions have
declined since 1970 in North America and Europe and somewhat later in eastern Europe and
80 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.
85 (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
90 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 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
95 precipitation pH. Base cations per se cannot neutralize acid precipitation, but carbonates,
hydroxides, and ammonia (NH_3) can. If the only or dominant substance entering the
atmosphere were SO_2 , then the relationship between $\text{SO}_4\text{-S}$ and H^+ would be stoichiometric,
and reducing 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
100 that does not settle out after coal burning in power plants) may contain sulfates and lime (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 H^+ . If fly ash contains predominantly salts, emissions controls will reduce SO_4-S and cations with negligible effects on rainfall H^+ . Only controls on SO_2 emissions should have positive and stoichiometric effects on rainfall 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. 2010, 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 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.

NH_3 is highly reactive in the atmosphere and can neutralize atmospheric acids by forming NH_4- containing aerosol salts, consuming a proton in the process, and can deposit rapidly to surfaces, including vegetation. 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 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 NH_3 emissions could be a significant source of a lack of stoichiometry between SO_4-S and H^+ , but this has not been quantified. Particularly in Europe, ceilings on emissions and management practices have been in place to reduce NH_3 loading to the atmosphere, but these vary regionally. The spatial and temporal scale of NH_4-N deposition is complicated by interactions between SO_2 , NO_3 and NH_3 . NH_3 preferentially forms one of several ammonium sulfate salts as an aerosol, which can be transported over longer distances than the reactive NH_3 phase, thus increasing the transport of both NH_4- and SO_4-S . Excess NH_3 can react with NO_3 , in the atmosphere, forming the NH_4NO_3 aerosol, which, although relatively labile, can increase the transport distance of both NH_4- and NO_3-N . If NH_3 levels exceed NO_x and SO_2 emissions, the reactive NH_3 is deposited more locally (Lehmann et al. 2007). Thus transport of NH_3 is partly determined by atmospheric concentrations of SO_2 and NO_3 , and declining SO_2 , for example, could cause more local deposition of reactive NH_3 .

Trends in emissions of SO_2 and cations, as well as NH_4- and NO_3 , vary regionally and change over time. Emissions of 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 to 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 SO₂ 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 ~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 SO₄-S and H⁺ were synchronous with changes in cation deposition; and (3) non-stoichiometric differences in SO₄-S and H⁺ could be explained by trends in cation, NH₄-N, or NO₃-N deposition. We also explored relationships between fossil energy use and patterns of H⁺, SO₄-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 (Figure 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 Convention on Long-Range Transboundary Air Pollution, 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). 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).

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

190 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
195 European countries (Austria, Czech Republic, Finland, France, Germany, Great Britain, Latvia,
Netherlands, Norway, Poland, Portugal, Russia, Spain, Sweden, and Switzerland) (Figure 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).

200 Anions and cations were closely balanced in most US states and European countries whose
records were initially selected (Figure 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 (Figure 2 a). Anions and cations were lower, and less
variable, in US states (Figure 2 b). Thus, data from Austria, France, Portugal, and Russia were
205 included in only some of the analyses.

Emissions controls

210 Since 1975, economic trends and changes in emission standards and technology have produced
regionally varying trends in global SO₂ emissions (Smith et al 2011). Given that electricity
generation since 1970 has been responsible for 50-67% of all SO₂ 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 SO₂ emissions (including using low S coal, washing coal, using scrubbers and other filter
control technology, and switching to natural gas or other energy sources).

215 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
220 houses collect dry salts and fly ash. In older plants, about 10% of fly ash was emitted; in newer
systems, less than 0.5% of fly ash is emitted. Phase I of the Clean Air Act Amendment of 1990
required SO₂ emission 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
225 being decommissioned, and plants are switching to alternate and cleaner fuels, suggesting that
SO₄-S and pH should still be changing slowly. However, patterns of SO₂ emissions in other
countries will not necessarily follow those of the US, given different legislation and emission
control technology, fuel use and quality, and the adoption of nuclear and other alternate
energy sources.

230 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. As of 2012, 50 European countries have ratified the 1979

235 Convention on Long-range Transboundary Air Pollution, but at different times. Fewer countries
240 ratified the 1985 Sulfur Protocol or the 1988 NO_x Protocol; 25 European countries and the US
245 ratified the most recent 1999 Gothenburg Protocol which set more stringent emission ceilings
for 2010. Although the Gothenburg protocol was expected to reduce NO_x emissions by
approximately 50%, reductions in NH₃ were expected to be much less (Erisman et al. 2003).
Thus the large (~50%) reductions in NH₃ emissions from Eastern Europe are more likely due to
240 major reductions in agricultural activity following the political changes of 1989-1990 (Lövblad et
al. 2004). European emissions of NH₃ are now regulated through the National Emission Ceiling
Directive (Skjoth and Geels 2013) and ceilings for different countries vary significantly. For
example, the Netherlands, with a high historic NH₃ emission load, has set a more stringent
245 reduction goal, with measures specifically targeting agricultural activities such as the covering
of outside manure storage tanks and the development of low-emission housing systems
(Mosquera et al. 2005, Erisman et al. 2003). However, uncertainties in calculating NH₃
emissions are high, and even very large estimated reductions in emissions have not always
250 been followed by measurable reductions in NH₄-N deposition (e.g. Horváth and Sutton 1998,
Horváth et al. 2009), possibly due to changes in transport distance due to changes in SO₂
concentrations. In the US, the EPA has the authority to require that concentrated animal
feeding operations (CAFOs) measure and control their NH₃ emissions, but ceilings have not
been established and only a few states have enacted regulations (EPA 2001, Merkel 2002).

255 In both the US and in Europe, transportation is the dominant source sector for NO_x emissions,
with 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 to 90
percent reduction in automobile NO_x. A 90 percent reduction of NO_x emissions from new diesel
260 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
NO_x to install and operate reasonably available control technology (RACT) by 1995, and the
Ozone Transport Commission (OTC) developed a cap and trade NO_x Budget Program. In New
England, these regulations have reduced NO_x from stationary sources by more than 50% from
265 1990 levels (EPA, 2012). Although the US pioneered both the technology and the regulation of
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 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,
270 and overall, NO_x emissions have decreased by 42% between 1990 and 2010.

Energy consumption trends

275 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) (Figure 3). From 1970 to
1990, all countries examined had increased total energy use. 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

280 exceptions where changes in fossil fuel consumption significantly trailed total energy growth (Figure 3a). From 1970-1990, 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. To a lesser extent, Switzerland and Spain increased fossil energy use, but total energy increased more rapidly, through development of other sources (e.g. nuclear energy).

285 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 ($y = 0.75x + 5.4$, $R^2 = 0.95$) (Figure 3b). 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.

295

Methods

Data collection

300 Precipitation chemistry. For each site, annual average records were obtained for all cations and anions, but most analyses focused on H⁺, SO₄-S, NO₃-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 ueq/L. Records from NADP were obtained in precipitation-weighted ueq/L.

310 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, it seems likely that relative trends in deposition inputs will be detected across sites using wet-only data.

320

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 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) vs. 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 to 1990 and 1990- to 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 SO₂ emissions in Eastern Europe (Smith et al. 2011).

To quantify the varying relationship between SO₄-S and H⁺, we compared the trends over time in SO₄-S to trends in H⁺. For each US state or European country the trend in SO₄-S and H⁺ was determined from slope term of a linear regression predicting concentration of the element (in ueq/L) vs. year. Trends were defined as stoichiometric for a given country or state if SO₄-S and 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 for SO₄-S and H⁺. If these regression models had a slope near 1, it indicated that trends in SO₄-S and 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 NH₃ must be considered in order to explain trends in H⁺ in precipitation, we corrected the trends over time in SO₄-S or H⁺, as follows. To

365 test how trends in Ca affected the stoichiometry of trends in $\text{SO}_4\text{-S}$ and H^+ , we compared the
trend in 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
370 in 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 H^+ was then tested (as for $\text{SO}_4\text{-S}$ and 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 and H^+ . We repeated this process to test how
trends in NH_3 and NO_3 affected the stoichiometry of trends in $\text{SO}_4\text{-S}$ and H^+ . We compared the
375 sum of the trends in $\text{NH}_4\text{-N}$ and H^+ to the sum of the trends in $\text{NO}_3\text{-N}$ and $\text{SO}_4\text{-S}$.

Results

Atmospheric chemistry and trends

380 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 $\text{SO}_4\text{-S}$,
385 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 to 71 ueq/L in Michigan, Ohio, Pennsylvania, and West Virginia, but
average values of $\text{SO}_4\text{-S}$ exceeded 95 ueq/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.

390 Before 1990, rainfall 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, Figure 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 H^+ in precipitation, compared to northern Europe and the US
395 (Table 1, Figure 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 (Figure 4b, 4c).

After 1990, precipitation became slightly less acidic in both the US and Europe, but peak H^+ in
the most severely affected US states was still greater than mean peak levels in Europe (Table 1).
400 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
405 $\text{SO}_4\text{-S}$ reached as high as 38 to 47 ueq/L in Michigan, Ohio, Pennsylvania, and West Virginia, but
average values of $\text{SO}_4\text{-S}$ exceeded 50 ueq/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

410 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.

415 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, Figure 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 H^+ in precipitation,
compared to northern Europe and the US (Table 1, Figure 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 $\text{SO}_4\text{-S}$
(Figure 4e, 4f).

420 From 1978 to 2010, concentrations of 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 (Figure 5). Even in locations where values of H^+ were quite low in the late
1970s (e.g., Oregon, Washington, Portugal, Spain) the concentration of H^+ declined significantly
425 from 1978-2010 ($p < 0.01$ for all countries and states except Latvia, $p < 0.03$ and Portugal, $p <$
 0.05) (Figure 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 H^+
(Figure 5 a, b, Table 2). From 1991 to 2010, most state and countries experienced significant
declines in H^+ ; H^+ did not change significantly in Oregon, Washington, Austria, France, Latvia,
430 Portugal, and Russia (Figure 5 a, 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.

435 Even in locations where values of $\text{SO}_4\text{-S}$ were quite low in the late 1970s (e.g., California,
Oregon, Washington) the concentration of $\text{SO}_4\text{-S}$ declined significantly from 1978-2010 ($p <$
 0.01 for all countries and states except Spain, $p < 0.03$ and Portugal, not significant) (Figure 5 c,
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,
440 Poland, Russia) experienced significant declines in $\text{SO}_4\text{-S}$ (Figure 5 c, 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 (Figure 5 c, d,
Table 3). In Europe, $\text{SO}_4\text{-S}$ declined significantly from 1991-2010 in all countries except Portugal
and Spain. In summary, declining trends in $\text{SO}_4\text{-S}$ emissions were more common than declining
445 trends in H^+ before 1990, but after 1991, both $\text{SO}_4\text{-S}$ and H^+ declined significantly except in the
western US and southern Europe and Russia.

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

At the beginning of the study period, NO_3-N in precipitation was higher in the most severely impacted countries of Europe compared to states in the US (Figure 5 g, h). No significant negative trends in NO_3-N were detected in the US or Europe before 1990. However, NO_3-N declined, though less steeply than SO_4-S , in the mid-Atlantic and northeast of the US after 1990 (Table 5, Figure 5g), while trends in NO_3-N in Europe were significantly negative for all countries except southern and northern Europe and Austria (Table 5, Figure 5h).

NH_4-N in precipitation was generally significantly higher in Europe compared to states in the US (Figure 5 i, j). The highest NH_4-N levels in Europe (60 to 90 $\mu\text{eq/L}$, Table 1) were four times as high as the highest levels in the US (15 to 25 $\mu\text{eq/L}$, Table 1). NH_4-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, SO_4-S was generally higher than NH_4-N , although concentrations (in μeq) tended to converge as levels of SO_4-S were reduced. In Europe, however, several countries (Austria, Czech Republic, Germany, Netherlands, Poland, Switzerland) reached the cross-over point (NH_4-N greater than SO_4-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 NH_3 emissions have reached near equal SO_4-S and NH_4-N concentrations since 2000.

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Trends in SO_4-S vs. H^+ . Trends in SO_4-S explained trends in H^+ in the US, but not in Europe (Table 7, Figure 6). Over the whole time period (1978-2010), SO_4-S increased only in Spain, and trends in H^+ were flat or negative everywhere (Table 7, Figure 6a). In the US, trends in H^+ were explained by trends in SO_4-S ($R^2 = 0.89$, $p < 0.0001$, Table 7), and the average trend in H^+ was exactly consistent with the average trend in SO_4-S ($\beta = 1.02$). In Europe, trends in H^+ were weakly related to trends in SO_4-S ($R^2 = 0.28$, $p < 0.05$), and trends in H^+ were much less negative than expected given trends in SO_4-S ($\beta = 0.29$).

Taking account of trends in Ca as well as trends in SO_4-S did not help explain trends in H^+ in Europe or the US from 1978 to 2010, but taking account of trends in NH_4-N , and NO_3-N did help (Table 7, Figure 6b). Adjusting trends in SO_4-S to account for trends in Ca reduced the explanatory power of the relationship with 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 H^+ were steeper than expected given trends in SO_4-S minus Ca ($\beta = 1.06$). On the other hand, adjusting trends in SO_4-S and H^+ to include trends in NH_4-N and NO_3-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 H^+ plus NH_4-N were less steep than expected given trends in SO_4-S plus NO_3-N ($\beta = 0.84$ [US] and $\beta = 0.61$ [Europe]) (Table 7). Similar results are evident for the period 1991 to 2010 (Table 7). Interestingly, inclusion of NH_4-N and NO_3-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 NH_3 and 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 SO_4-S in precipitation vs. changes in energy consumption. In any given year where data were available, SO_4-S in precipitation was at best weakly related to fossil fuel consumption per unit area (Figure 7abc). Before 1990, trends in SO_4-S were weakly related to trends in fossil fuel use (Figure 7d), even though many countries had increased fossil fuel consumption but decreased SO_4-S in precipitation. After 1990 there was no relationship between changes in SO_4-S and changes in fossil fuel use (Figure 7e), as almost all countries showed decreased SO_4-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 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_3 , as well as differing natural sources of cations.

Over the >30-yr period of NADP and EMEP records (1978-2010), precipitation pH and SO_4-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_4-S and H^+ differed markedly between the US and Europe. For any given level of S in precipitation, H^+ 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. 2005), and is enriched in calcite with very little gypsum (Loye-Pilot et al. 1986). These natural carbonates are capable of neutralizing 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 NH_3 , which neutralize precipitation acidity, compared to the US.

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More locally derived dust can also affect precipitation chemistry. 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 H^+). We expected similar effects in arid regions of the US, and even expected to see more local effects of land management change. 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. However, there were no significant trends in Ca since 1978 in any of the western states examined in this study. Moreover, known patterns of logging activity in the Pacific Northwest in the last 30 years could not be discerned from precipitation data in our western states, in part because the slight decreases in Ca in precipitation, coincident with decreased logging road development, cannot be separated from the overall pattern of decreasing Ca in precipitation across the US. It is also possible that 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 (Vickers and Sickman 2011, Yu et al. 2012).

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During the first time period before 1990, many US states (9 of 13 reported) and most European countries had less negative trends in H^+ than in $\text{SO}_4\text{-S}$, the pattern reported by Hedin et al. (1994) and shown in Figure 6. This pattern was most significant in eastern European countries, a region with the highest $\text{SO}_4\text{-S}$ and H^+ loading in Europe, and to a lesser extent, states in the US that were also most significantly impacted by acid rain. This lack of stoichiometry between $\text{SO}_4\text{-S}$ and H^+ could be due either to declining inputs of alkaline dust and/or NH_3 , or else to emissions controls that reduce alkaline and/or S-containing particulates. 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 $\text{SO}_4\text{-S}$ than H^+ . 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^+ and $\text{SO}_4\text{-S}$ 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.

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After 1990 in the US, trends in H^+ in the US were more negative than expected based on declines in $\text{SO}_4\text{-S}$, the exact opposite pattern of that described by 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 $\text{NH}_4\text{-N}$) increased slightly in the midwest US (Lehmann et al. 2007), but not in most sites used in this study. Recent increases in $\text{NH}_4\text{-N}$ 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

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585 produce larger concentrated amounts of waste with larger emission factors (Merkel 2002). In addition, $\text{NO}_3\text{-N}$ 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.

590 The pattern of steeper than expected decline in H^+ in precipitation was not observed in Europe (except in Great Britain, where $\text{NO}_3\text{-N}$ and $\text{NH}_4\text{-N}$ declined, and Ca did not change, after 1990). Instead, declines in $\text{SO}_4\text{-S}$ remained steeper than H^+ after 1990 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 $\text{NO}_3\text{-N}$ in precipitation. Although particulate control measures that could reduce S-containing particulates (and cations) 595 in deposition were still taking effect after 1990 in Europe, our analysis suggests that the non-stoichiometric trends in H^+ and $\text{SO}_4\text{-S}$ were also significantly affected by sharp declines in NH_3 emissions, as well as declines in $\text{NO}_3\text{-N}$, 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 (Austria, Czech Republic, Germany, the Netherlands, and Poland, which had the steepest declines in $\text{NO}_3\text{-N}$ and $\text{NH}_4\text{-N}$. 600

605 There were other differences in patterns of precipitation chemistry between the US and European countries. We saw regionally steep declines in $\text{SO}_4\text{-S}$ in those US states most affected by acid precipitation after 2005, a pattern not observed in European countries. In Europe, declines in $\text{SO}_4\text{-S}$ and H^+ were generally observed before 2000 and could be traced back to patterns of energy use. For example, eastern European countries (Poland, Hungary, Czechoslovakia) showed sharp declines immediately after the fall of the Soviet Union, a period 610 of declining industrial activity.

The significant declines in $\text{NO}_3\text{-N}$ observed in the US since 1991 are likely explained both by changes in the transportation industry (catalytic converters) and changes for industrial emissions. Nevertheless, despite declines, $\text{NO}_3\text{-N}$ in precipitation in 2007-2010 remained higher 615 in most eastern European and some western European countries than anywhere in the US, perhaps because of differences in transportation patterns and population density.

620 There was no clear relationship between the concentration of $\text{SO}_4\text{-S}$ 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 $\text{SO}_4\text{-S}$ 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 $\text{SO}_4\text{-S}$ in precipitation, while countries with smaller increases in fossil fuel use showed declining $\text{SO}_4\text{-S}$ in precipitation. After 1990, however, all countries showed declining $\text{SO}_4\text{-S}$ in precipitation, and $\text{SO}_4\text{-S}$ trends were not explained by trends in fossil energy use, suggesting that emission controls overwhelmed fossil fuel use effects on precipitation chemistry. For 625

630 example, after 1990, SO₄-S declined in Czechoslovakia, Germany, and Poland, where fossil fuel consumption also declined, but SO₄-S declined even more steeply in The Netherlands, where fossil fuel use increased.

635 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 1978-2010, 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 SO₄-S. Starting in 1991, in contrast, Ca declined in European countries (especially eastern Europe) where SO₄-S and H⁺ also continued to decline.

645 Hedin et al. (1994) and others have speculated that declines in particulate emissions were responsible for the slower decline of H⁺ compared to SO₄-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⁺ and SO₄-S was remarkably good in the US, and adding in cations, or NH₄-N, did not significantly improve correlations between the two. In many parts of Europe, however, declines in SO₄-S were significantly greater than declines in H⁺, and accounting for declines in Ca (as a proxy for basic particles that could neutralize acidity) did not completely explain the lack of stoichiometry; declining NH₄-N was needed to improve trend analyses. In Europe, declining NH₃ emissions had the paradoxical effect of appearing to slow declines in precipitation H⁺, although the reduction in NH₄-N deposition certainly has significant and positive ecological effects.

660 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 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 et al. 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 NO₃-N and NH₄-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.

675 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 $\text{SO}_4\text{-S}$
680 and cations. In Europe, significant declines in NH_3 emissions contributed to a lack of
stoichiometry between $\text{SO}_4\text{-S}$ and H^+ in precipitation. Continued efforts to control SO_2 and NO_x
emissions should result in more sustained and stoichiometric decreases in H^+ as well.

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
685 1991-2010 (the era marked by the collapse of eastern Europe economies, 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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Table 1. Average values of pH, Ca, SO4-S, NO3-N, and NH4-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. Values are in ueq/L except for pH. Record lengths vary among countries and among properties (see Tables 2 to 6).

State/Country	Site name	code	pH		Ca		SO4-S		NO3-N		NH4-N	
			≤ 1990	≥ 1991	≤ 1990	≥ 1991	≤ 1990	≥ 1991	≤ 1990	≥ 1991	≤ 1990	≥ 1991
<u>United States</u>												
Arizona	Oliver Knoll	AZ99*	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
<u>Europe</u>												
Austria	Illmitz	AT02*	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**	Donon	FR08		4.9		8.9		23.7		22.2		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*	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
Switzerland	Payerne	CH02	4.8	5.2	18.2	16.7	45.8	21.8	27.0	20.9	39.4	34.7
U.K./ Gt. Britain	High Muffles	GB14	4.2	4.6	13.6	14.8	75.6	50.4	37.8	31.5	48.0	36.9

* Ca data has large variability: AZ99: 3 to 4 fold spikes in Ca in 1984, 1990, 1996, 2001. AT02: cation records appear unreliable, likely a strong agricultural signal. PT01: 5-fold spikes in Ca in 2001, 2005, 2009.

** The FR08 record begins in 1990.

Table 2. Trends in H+ for all years, before 1990, and since 1990, for available record. Bold font indicates trend is significant at $p < 0.01$. Units are ueq/L.

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

Table 3. Trends in SO4-S for all years, before 1990, and since 1990, for available record. Bold font indicates trend is significant at $p < 0.01$. Units are ueq/L.

Site	SO4-S trend		to 1990		after 1990		record length
	all years slope	p <	slope	p <	slope	p <	
United States							
AZ99	-1.19	0.00	-5.18	0.04	-0.36	0.01	1981-2010
CA99	-0.14	0.00	0.23	0.47	-0.04	0.39	1981-2010
CO99	-0.60	0.00	-1.22	0.14	-0.37	0.01	1981-2010
GA41	-0.61	0.00	-0.91	0.09	-0.49	0.02	1979-2010
MI26	-1.47	0.00	-1.55	0.02	-1.21	0.00	1979-2010
MN16	-0.54	0.00	-0.92	0.02	-0.25	0.02	1978-2010
NC25	-0.50	0.00	-0.23	0.57	-0.33	0.08	1978-2010
NH02	-0.97	0.00	-0.99	0.02	-1.12	0.00	1978-2010
NY20	-0.93	0.00	-0.22	0.74	-0.98	0.00	1978-2010
OH71	-1.48	0.00	-0.65	0.10	-1.82	0.00	1978-2010
OR10	-0.09	0.00	-0.29	0.00	0.00	0.94	1980-2010
PA29	-1.31	0.00	-1.05	0.05	-1.22	0.00	1978-2010
WA14	-0.06	0.00	-0.24	0.01	0.04	0.04	1980-2010
WV18	-1.43	0.00	-0.74	0.33	-1.52	0.00	1978-2010
Europe							
AT02	-3.10	0.00	1.04	0.61	-2.67	0.00	1978-2009
CH02	-1.65	0.00	-1.51	0.20	-1.22	0.00	1984-2008
CZ01	-4.75	0.00	-3.87	0.07	-2.82	0.00	1978-2007
DE02	-3.04	0.00	-0.02	0.99	-2.31	0.00	1982-2008
ES01_15	0.63	0.03	4.14	0.08	0.33	0.41	1984-2007
FI04	-1.38	0.00	-1.43	0.01	-0.88	0.00	1978-2009
FR08					-0.96	0.00	1990-2008
GB14	-2.19	0.00	-4.93	0.28	-2.17	0.00	1987-2009
LV10	-2.23	0.00	1.91	0.35	-2.66	0.00	1985-2009
NL02_09	-2.36	0.00	4.50	0.02	-3.01	0.00	1978-2009
NO01	-1.85	0.00	-2.05	0.00	-1.51	0.00	1978-2010
PL01_05	-3.95	0.00	-3.16	0.00	-2.77	0.00	1978-2009
PT01	-0.38	0.18	1.38	0.43	0.21	0.55	1979-2008
RU01	-0.99	0.00	-3.23	0.03	-0.05	0.82	1980-2009
SWDO	-1.71	0.00	-1.19	0.30	-1.13	0.00	1983-2008

10 Table 4. Trends in Ca for all years, before 1990, and since 1990, for available record. Bold font indicates trend is significant at $p < 0.01$. Units are $\mu\text{eq/L}$.

Site	Ca trend all years		to 1990		after 1990		record length
	slope	p <	slope	p <	slope	p <	
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	-0.08	0.00	-0.27	0.03	0.02	0.64	1979-2010
MI26	-0.14	0.00	-0.30	0.09	-0.01	0.88	1979-2010
MN16	-0.08	0.02	-0.37	0.00	-0.25	0.02	1978-2010
NC25	-0.03	0.14	-0.10	0.41	0.04	0.19	1978-2010
NH02	-0.08	0.00	-0.27	0.00	0.00	0.87	1978-2010
NY20	-0.08	0.00	-0.12	0.25	-0.01	0.69	1978-2010
OH71	-0.10	0.00	-0.34	0.01	-0.06	0.26	1978-2010
OR10	-0.01	0.57	-0.08	0.02	0.05	0.04	1980-2010
PA29	-0.09	0.00	-0.21	0.04	-0.06	0.11	1978-2010
WA14	-0.01	0.58	-0.11	0.07	0.05	0.00	1980-2010
WV18	-0.19	0.00	-0.37	0.07	-0.09	0.04	1978-2010
Europe							
AT02	-5.71	0.00	-6.84	0.50	-5.60	0.00	1987-2009
CH02	-0.24	0.09	-0.27	0.64	-0.44	0.10	1984-2008
CZ01	-1.00	0.00	-4.34	0.04	-0.74	0.02	1986-2007
DE02	-0.73	0.00	1.25	0.05	-1.16	0.00	1983-2008
ES01_15	0.54	0.14	0.11	0.97	1.70	0.00	1985-2007
FI04	-0.15	0.00	-1.20	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	-1.36	0.00	-0.40	0.86	-1.86	0.00	1985-2009
NL02_09	-0.10	0.60	-0.95	0.08	-0.75	0.10	1978-2009
NO01	-0.18	0.00	-0.22	0.06	-0.06	0.11	1978-2010
PL01_05	-1.03	0.00	0.02	0.96	-1.26	0.00	1978-2009
PT01	2.70	0.04			2.67	0.11	1989-2009
RU01	-1.33	0.01	-9.84	0.00	0.16	0.70	1982-2009
SWDO	0.10	0.09	0.05	0.83	0.37	0.00	1983-2008

15 Table 5. Trends in NO₃-N for all years, before 1990, and since 1990, for available record. Bold font indicates trend is significant at p < 0.01. Units are ueq/L.

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

20 Table 6. Trends in NH₄-N for all years, before 1990, and since 1990, for available record. Bold font indicates trend is significant at p < 0.01. Units are ueq/L.

Site	NH ₄ -N trend		to 1990		after 1990		record length
	all years		slope	p	slope	p	
	slope	p	slope	p	slope	p	
United States							
AZ99	0.30	0.00	-0.30	0.60	0.48	0.00	1981-2010
CA99	0.00	0.97	1.38	0.04	0.03	0.80	1981-2010
CO99	0.16	0.00	0.21	0.51	0.17	0.07	1981-2010
GA41	0.15	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	-0.02	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	-0.40	0.03	1.68	0.34	-0.55	0.02	1984-2008
CZ01	-0.82	0.01	1.17	0.26	-0.80	0.29	1978-2007
DE02	-0.76	0.00	0.29	0.82	-0.34	0.18	1982-2008
ES01_15	1.24	0.00	1.84	0.15	1.90	0.00	1984-2007
FI04	-0.48	0.00	0.19	0.64	-0.29	0.04	1980-2009
FR08					-1.48	0.00	1990-2008
GB14	-0.69	0.01	-3.36	0.33	-0.45	0.19	1987-2009
LV10	-0.35	0.13	-2.28	0.41	-0.71	0.03	1986-2009
NL02_09	-1.47	0.01	6.20	0.00	-2.48	0.00	1978-2010
NO01	-0.70	0.00	-0.44	0.21	-0.64	0.00	1978-2010
PL01_05	-2.08	0.00	-1.92	0.21	-1.25	0.00	1978-2009
PT01	0.41	0.08	-0.12	0.86	1.35	0.02	1979-2009
RU01	0.38	0.02			0.44	0.07	1986-2009
SWDO	-0.41	0.02	0.58	0.65	-0.01	0.96	1983-2008

25 Table 7. Regression models relating (1) trends in H+ to trends in SO4-S, (2) trends in H+ to
 trends in SO4-S adjusted for Ca, and (3) trends in H+ plus NH4-N to trends in SO4-S plus NO3-N,
 for 14 states in the US and 14 countries in Europe. Trends in H+ in the US are stoichiometric:
 they are significantly related to trends SO4-S in all periods (1978-2010, 1978-1990, 1991-2010).
 30 The inclusion of NO3-N and NH4-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 SO4-S in any period. Adjusting the trends in SO4-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 NO3-N and NH4-N
 produces a significant relationship.

35

	All years			Since 1990		
	r ²	beta	p < ¹	r ²	beta	p < ¹
United States						
SO4-S vs. H+	0.89	1.02	0.00	0.98	1.23	0.00
SO4-S minus Ca vs. H+	0.83	1.06	0.00	0.93	1.24	0.00
SO4-S plus NO3-N vs. H+ plus NH4-N	0.93	0.84	0.00	0.98	0.89	0.00
Europe						
SO4-S vs. H+	0.28	0.29	0.05	0.17	0.27	0.13
SO4-S minus Ca vs. H+	0.08	0.13	0.32	0.22	0.27	0.08
SO4-S minus Ca vs. H+ ²	0.21	0.32	0.13	0.40	0.74	0.02
SO4-S plus NO3-N vs. H+ plus NH4-N	0.67	0.61	0.00	0.66	0.71	0.00

¹ P-values of beta (slope of the regression).

² regression based on removal of two outliers (AT02, PT01).

Table 8. Interannual variability in precipitation chemistry. Correlations of annual values in precipitation of (1) H+ vs. SO4-S, (2) H+ vs. SO4-S minus Ca, and (3) H+ plus NH4-N vs. SO4-S plus NO3-N, over periods of record, at 14 states in the US and 14 countries in Europe. Bold font indicates site at which inclusion of NO3-N and NH4-N improved correlation by more than 0.2.

45

	SO4-S vs. H+	SO4-S minus Ca vs. H+	SO4-S plus NO3-N vs. H+ plus NH4-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	0.72
DE02	0.92	0.88	0.95
ES01	-0.58	-0.31	0.74
FI04	0.93	0.55	0.97
FR08	0.26	0.37	0.94
GB14	0.88	0.94	0.95
LV10	0.88	0.94	0.95
NL02_09	0.37	0.31	0.60
NO01	0.61	0.62	0.96
PL01_05	0.66	0.64	0.92
PT01	0.07	0.14	-0.08
RU01	0.73	-0.23	0.11
SWDO	0.90	0.94	0.97

Figure captions

Figure 1. (a) Locations of fifteen sites in Europe with long-term precipitation chemistry records used in this study. Records are from the EMEP Program (Co-operative Programme for Monitoring and Evaluation of the Long-range Transmission of Air Pollutants in Europe) (<http://www.nilu.no/projects/ccc/sitedescriptions/index.html>) and from IVL Swedish Environmental Research Institute (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.

Figure 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 Figure 1. European countries are Austria (AT), Switzerland (CH), Czech Republic (CZ), Germany (DE), Spain (ES), Finland (FI), France (FR), Great Britain (GB), Latvia (LV), Netherlands (NL), Norway (NO), Poland (PL), Portugal (PT), Russia (RU), and Sweden (SW). States are Arizona (AZ), California (CA), Colorado (CO), Georgia (GA), Michigan (MI), Minnesota (MN), New Hampshire (NH), New York (NY), North Carolina (NC), Ohio (OH), Oregon (OR), Pennsylvania (PA), and Washington (WA).

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

Figure 4 (a). Relationship between average SO₄-S and H⁺ (a), (d), Ca (b), (e), and NH₄-N (c), (f) in precipitation before (a to c) and after 1990 (d to f) in Europe (closed circles, solid line) and the US (open circles, dashed line) (a) H⁺ and SO₄-S, 1978 to 1990. H⁺ was closely related to SO₄-S in the US ($r^2 = 0.88$) and almost 1:1, but in Europe SO₄-S values were more variable and considerably higher than H⁺ ($r^2 = 0.37$). (b) Ca and SO₄-S, 1978 to 1990. Ca in precipitation was much higher in Europe than in the US, except for northern Europe (FI, NO, SW, GB). (c) NH₄-N and SO₄-S, 1978 to 1990. NH₄-N in precipitation was much higher in Europe, and more closely related to SO₄-S ($r^2 = 0.82$) than in the US ($r^2 = 0.63$). (d) H⁺ and SO₄-S, 1991-2010. H⁺ was closely related to SO₄-S in the US ($r^2 = 0.87$) and near 1:1, but in Europe SO₄-S values were considerably higher and were not related to H⁺ ($r^2 = 0.09$). (e) Ca and SO₄-S, 1991 to 2010. Ca in precipitation in Europe was much higher in Europe than in the US, except for northern Europe (FI, FR, NO, SW). (f) NH₄-N and SO₄-S, 1991 to 2010. NH₄-N in precipitation was much higher in Europe, nearly 1:1 with SO₄-S, and more closely related to SO₄-S ($r^2 = 0.65$) than in the US ($r^2 = 0.53$).

Figure 5. Trends from 1978-2010 in (a) H⁺ in the US, (b) H⁺ in Europe, (c) SO₄-S in the US, (d) SO₄-S in Europe, (e) Ca in the US (f) Ca in Europe, (g) NO₃-N in the US, (h) NO₃-N in Europe, (i)

NH₄-N in the US, (h) NH₄-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).

Figure 6. Trends in (a) H⁺ in precipitation as a function of trends in SO₄-S in precipitation (ueq/yr), in the US and European countries, (b) H⁺ as a function of trends in SO₄-S minus Ca, and (c) H⁺ plus NH₄-N as a function of trends in SO₄-S plus NO₃-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 SO₄-S is less negative or more positive than the trend in H⁺, and points above the line are cases in which the trend in SO₄-S is more negative or less positive than the trend in H⁺.

Figure 7 (abc). Countries with higher fossil energy use per unit area also had higher SO₄-S in precipitation, although the relationship is strongest in 1990 and highly dependent on one high outlier country (Netherlands), and becomes quite weak by 2000. (d), (e) Trends in SO₄-S in precipitation as a function of trends in fossil energy use per unit area, 1970-1990 (d) and 1990-2005 (e).

Fig. 1a.

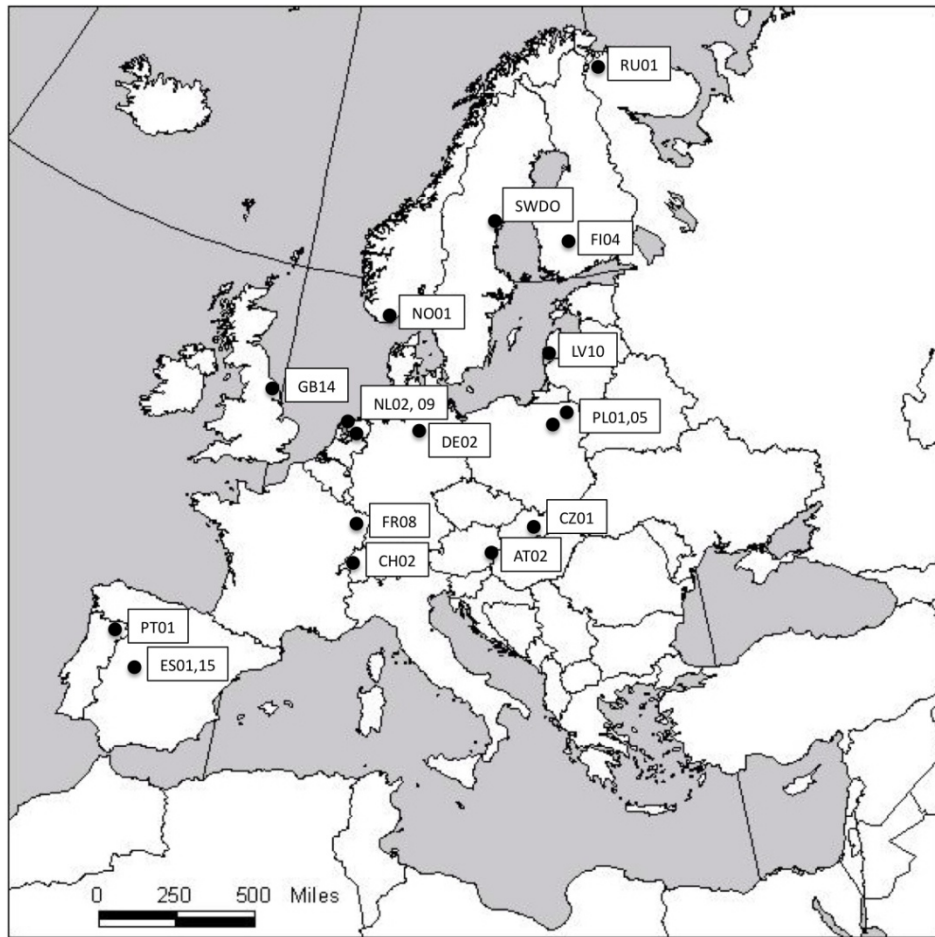


Fig. 1a

Fig. 1b.

Fig. 1b

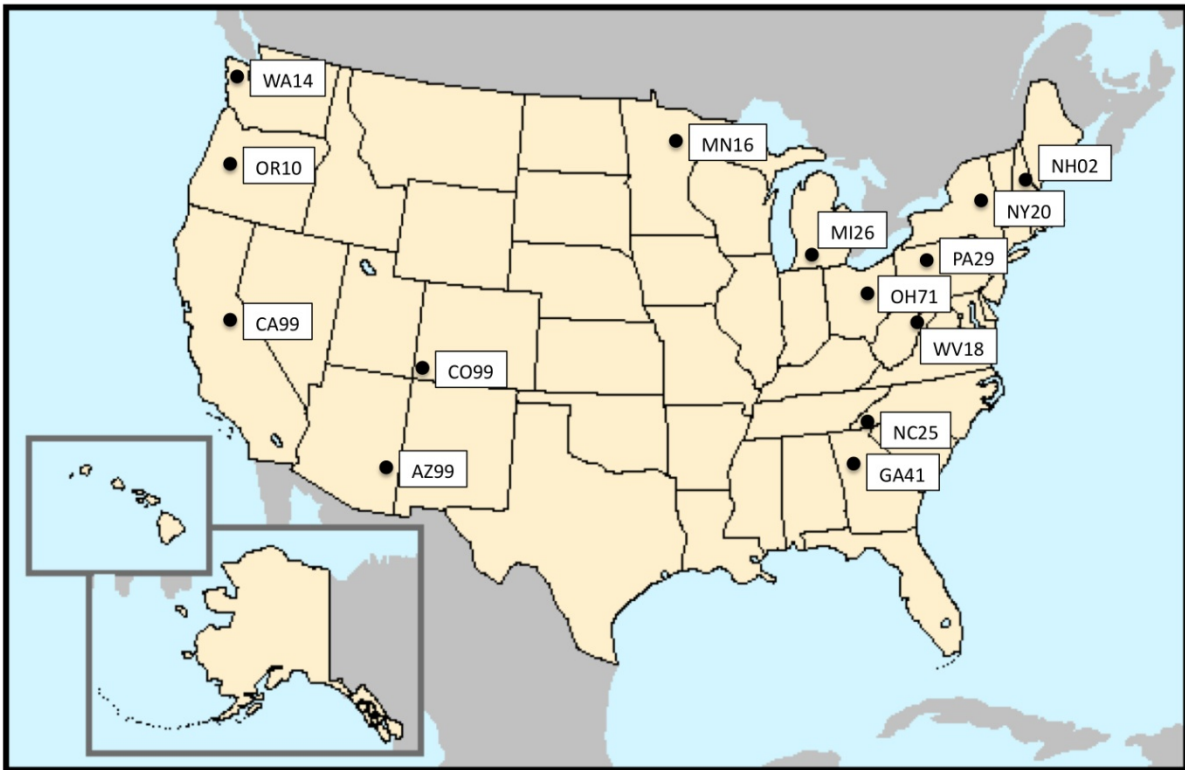


Fig. 2a.

Fig. 2 (a)

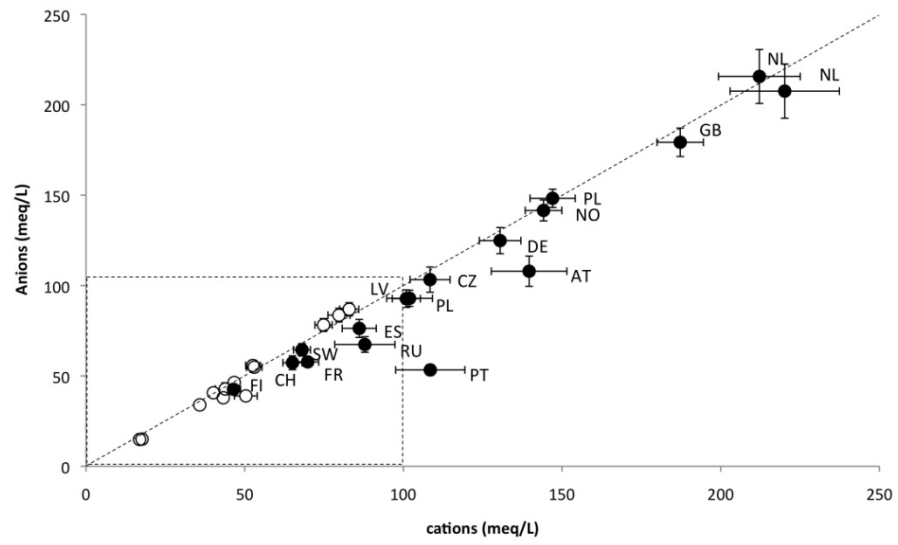


Fig. 2b.

Fig. 2 (b)

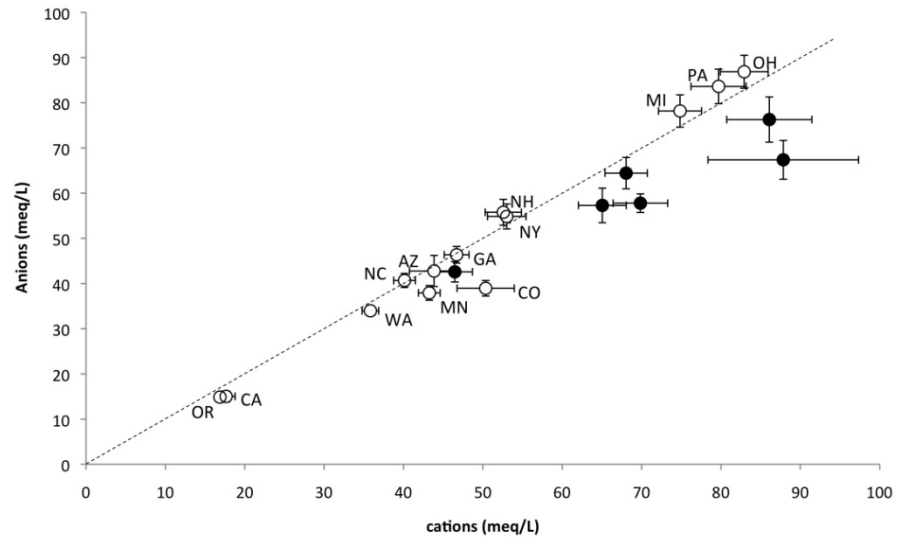


Fig. 3.

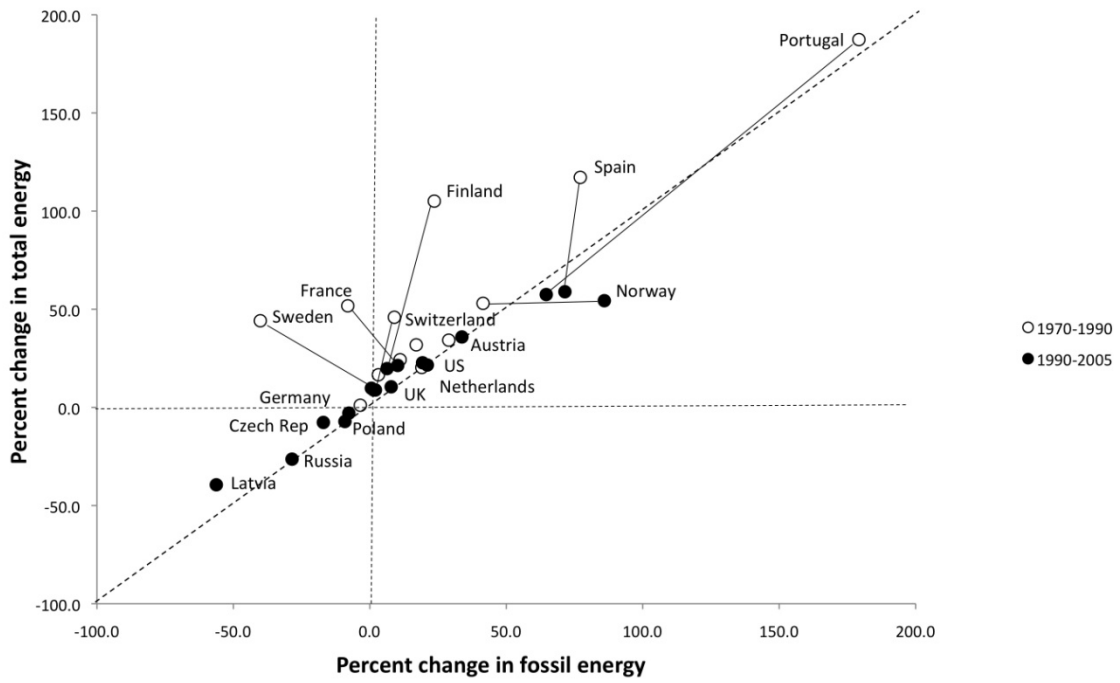


Fig 4a.

Fig 4 a

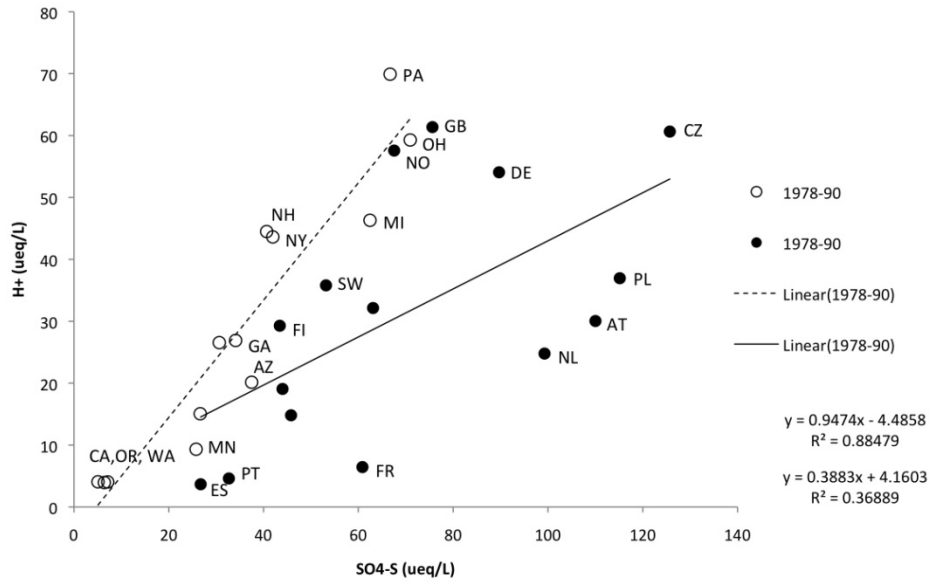


Fig. 4b.

Fig 4 b

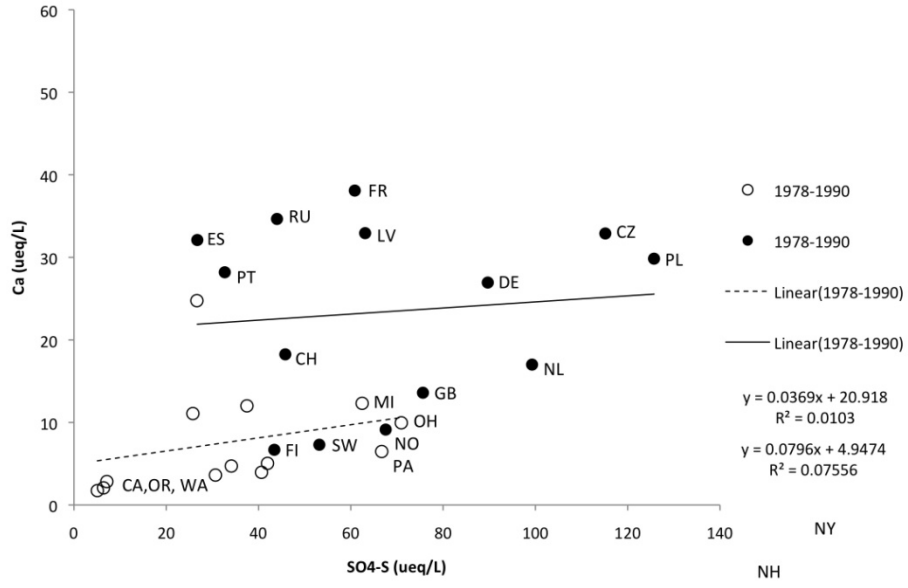


Fig. 4c.

Fig 4 c

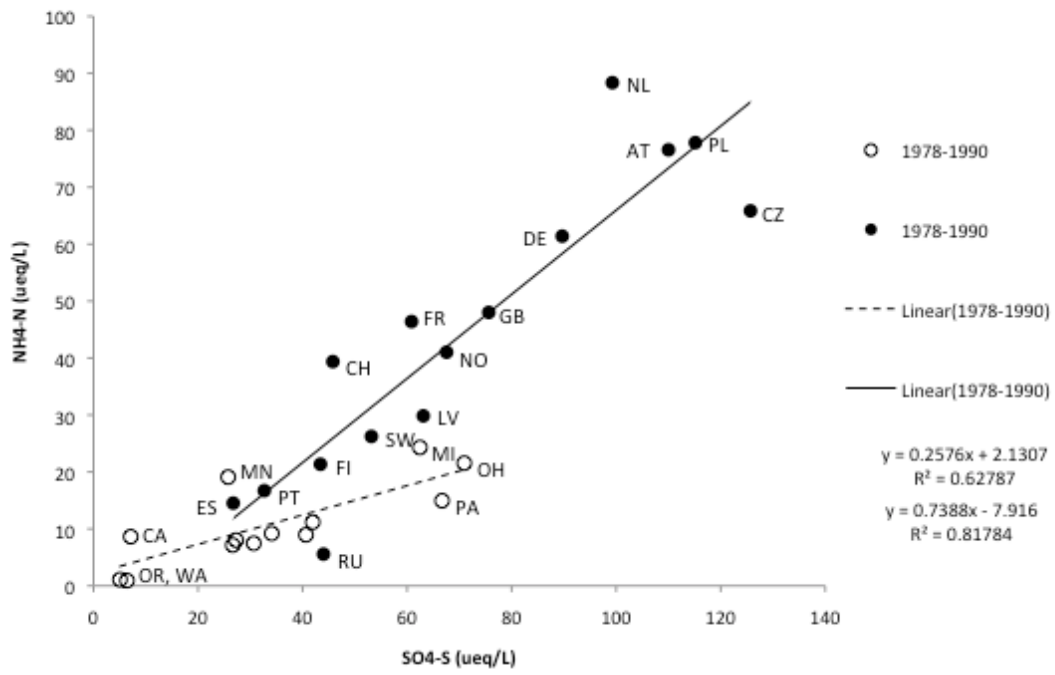


Fig. 4d.

Fig 4 d

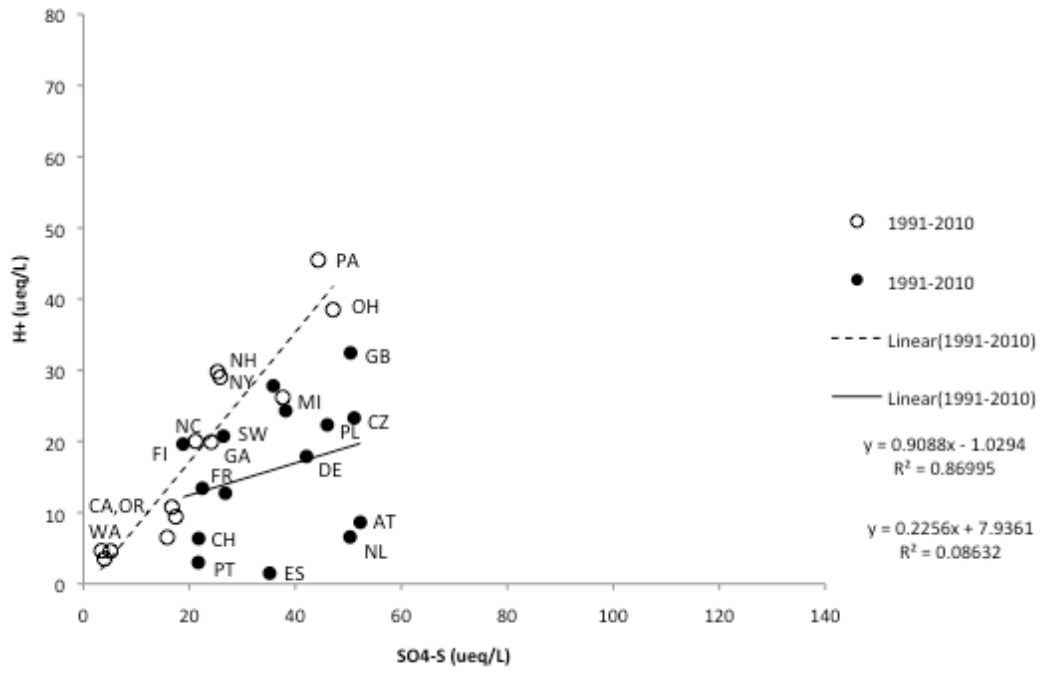


Fig. 4e.

Fig 4 e

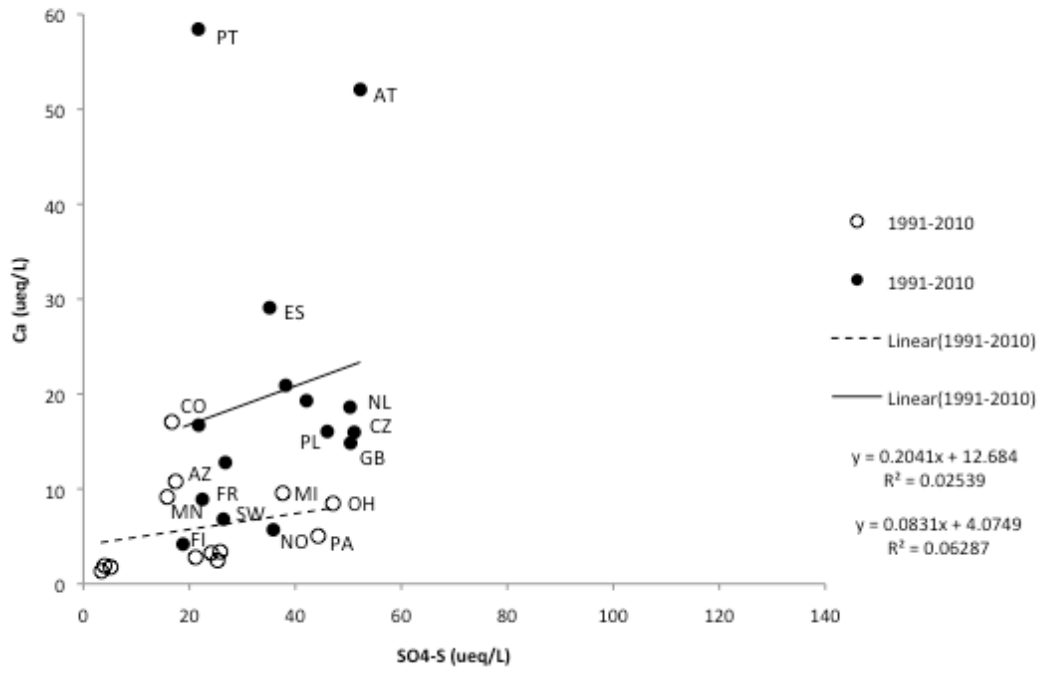


Figure 4f.

Fig 4 f

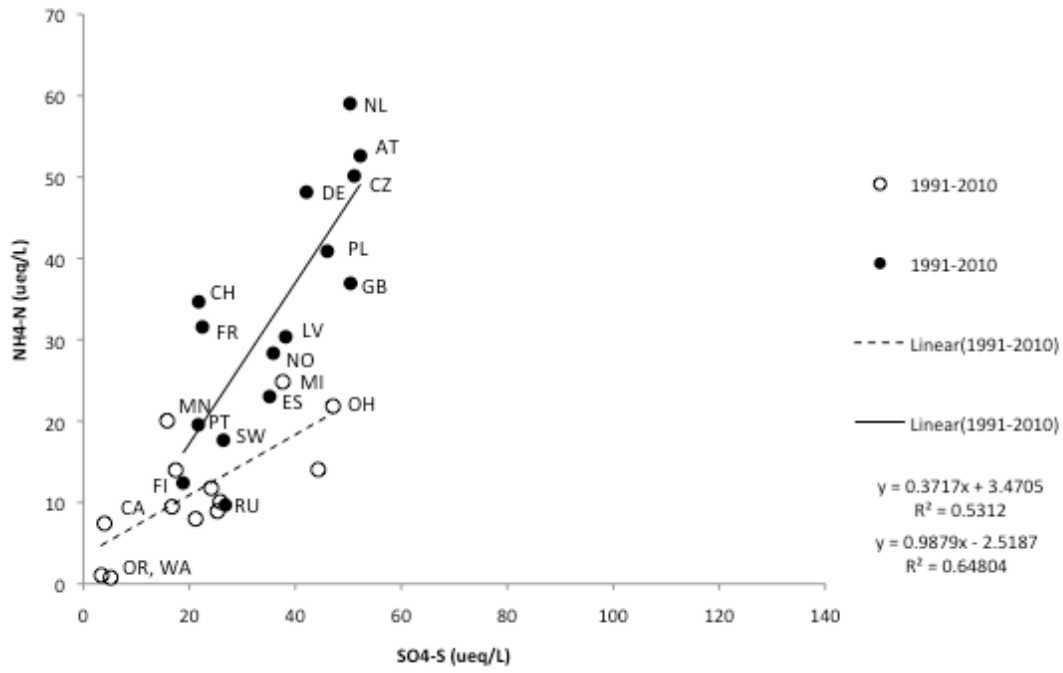


Fig. 5a.

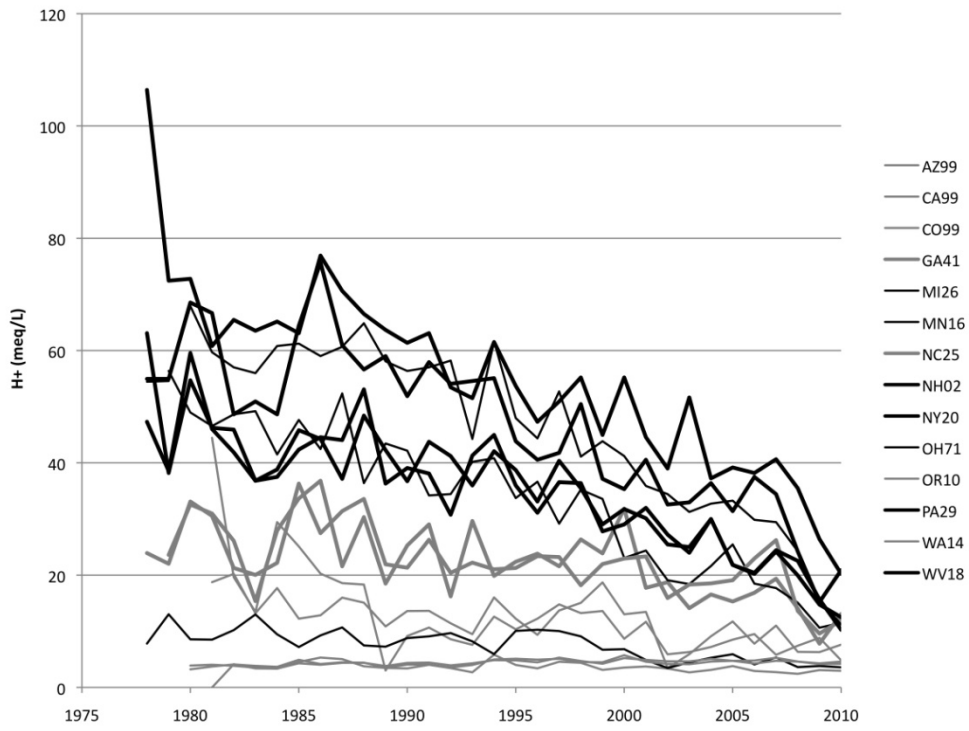


Fig. 5 (a)

Fig. 5b.



Fig. 5 (b)

Fig. 5c.

Fig. 5 (c)

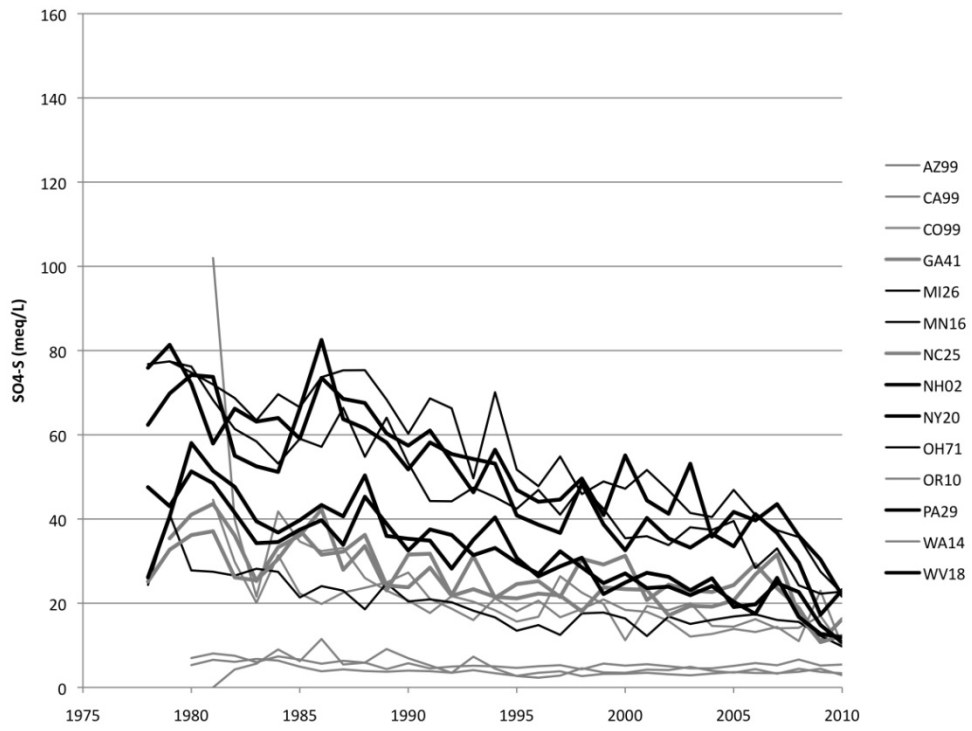


Fig. 5d.

Fig. 5 (d)

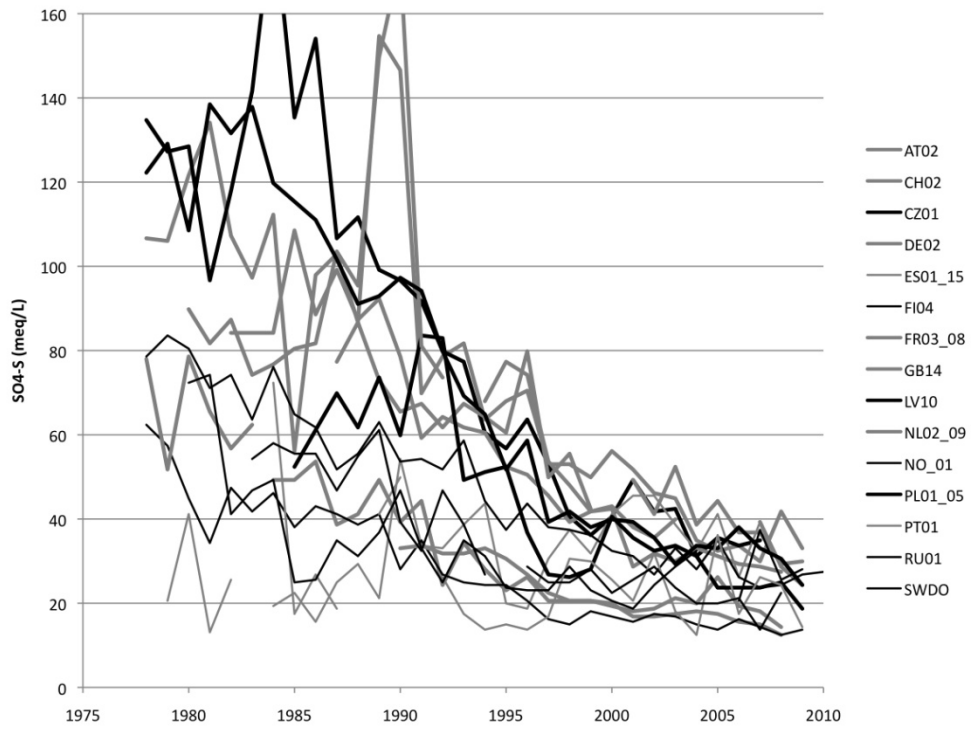


Fig. 5e.

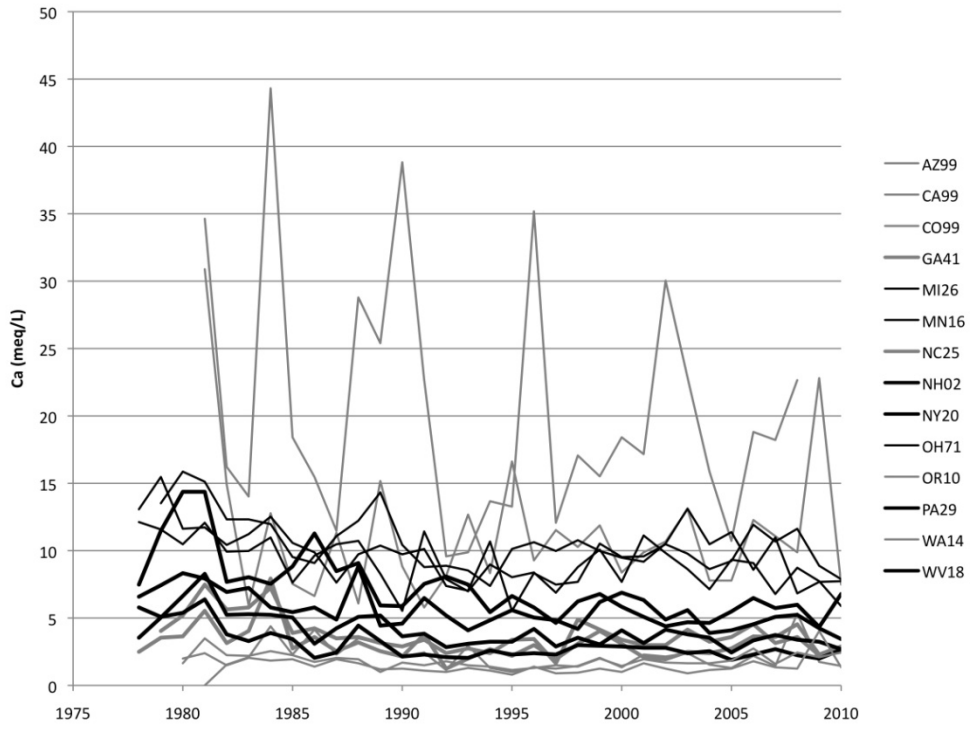


Fig. 5 (e)

Fig. 5f.

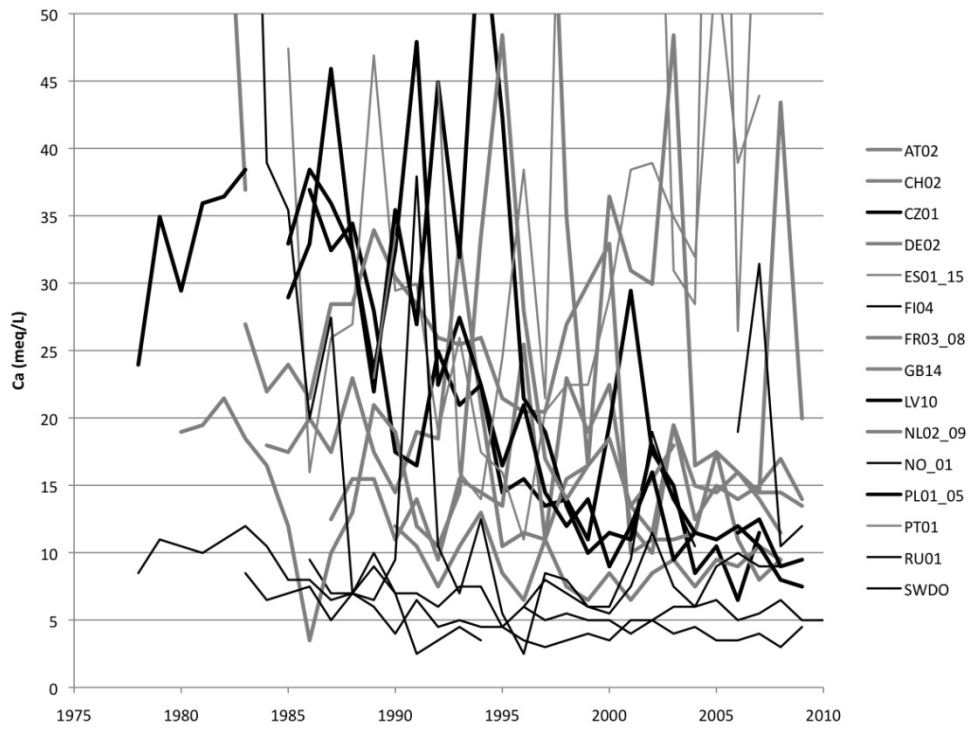


Fig. 5 (f)

Fig. 5g.

Fig. 5 (g)

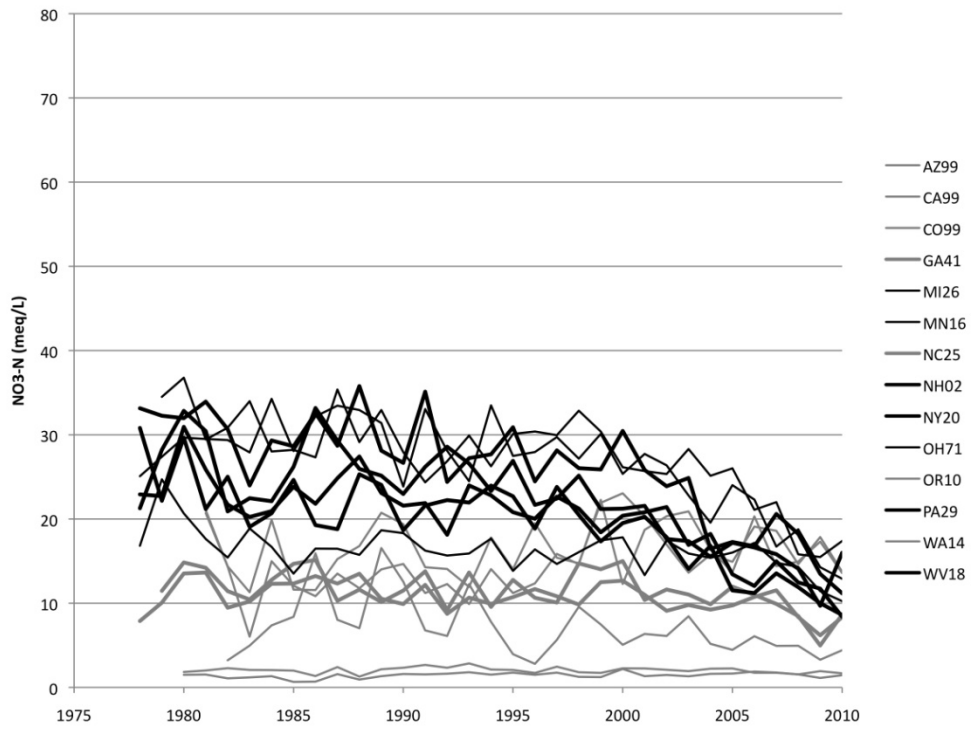


Fig. 5h.

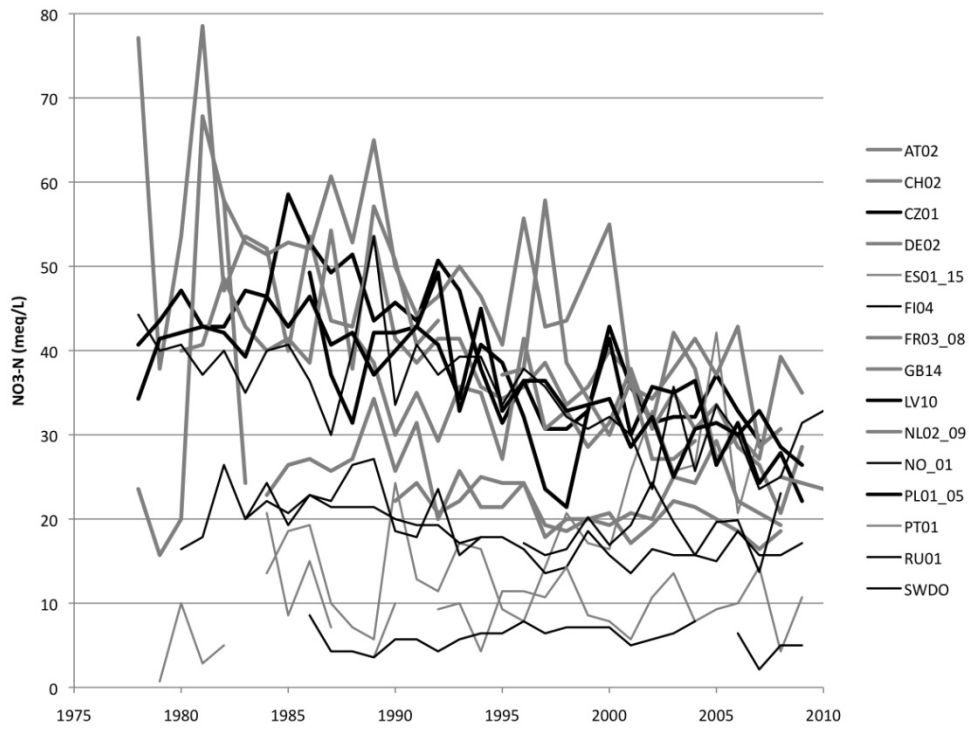


Fig. 5 (h)

Figure 5i.

Fig. 5 (i)

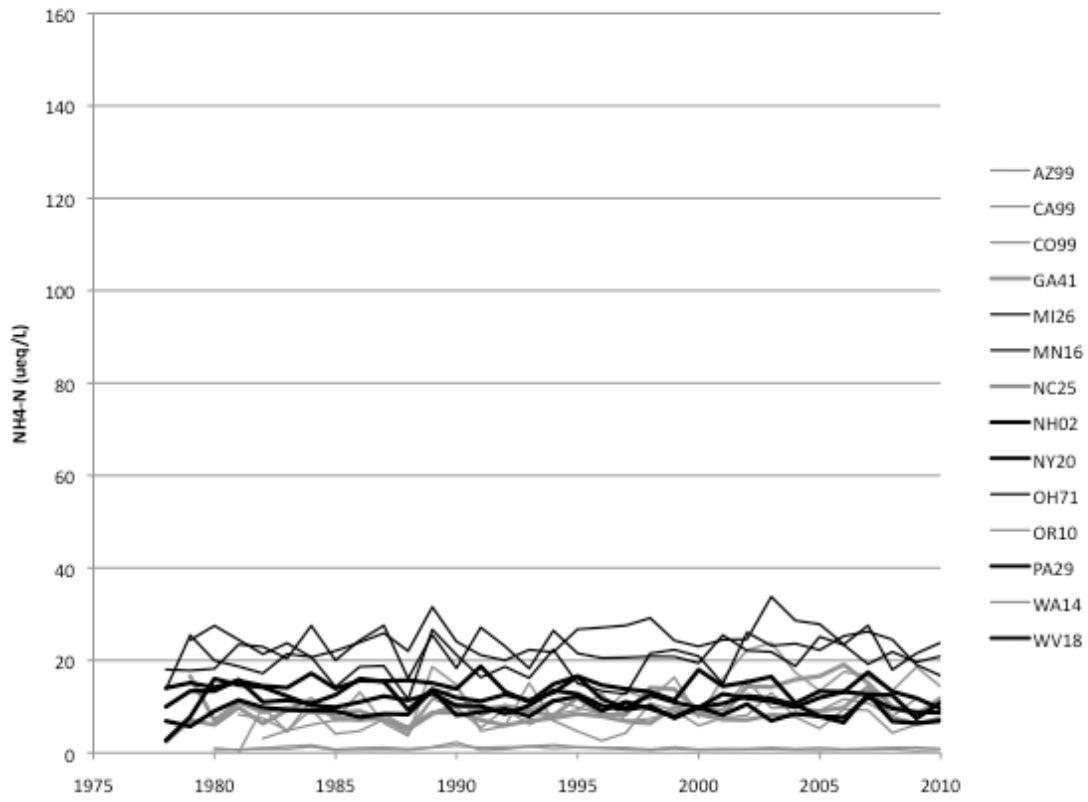


Figure 5j.

Fig. 5 (j)



Fig. 6a.

Fig. 6 (a)

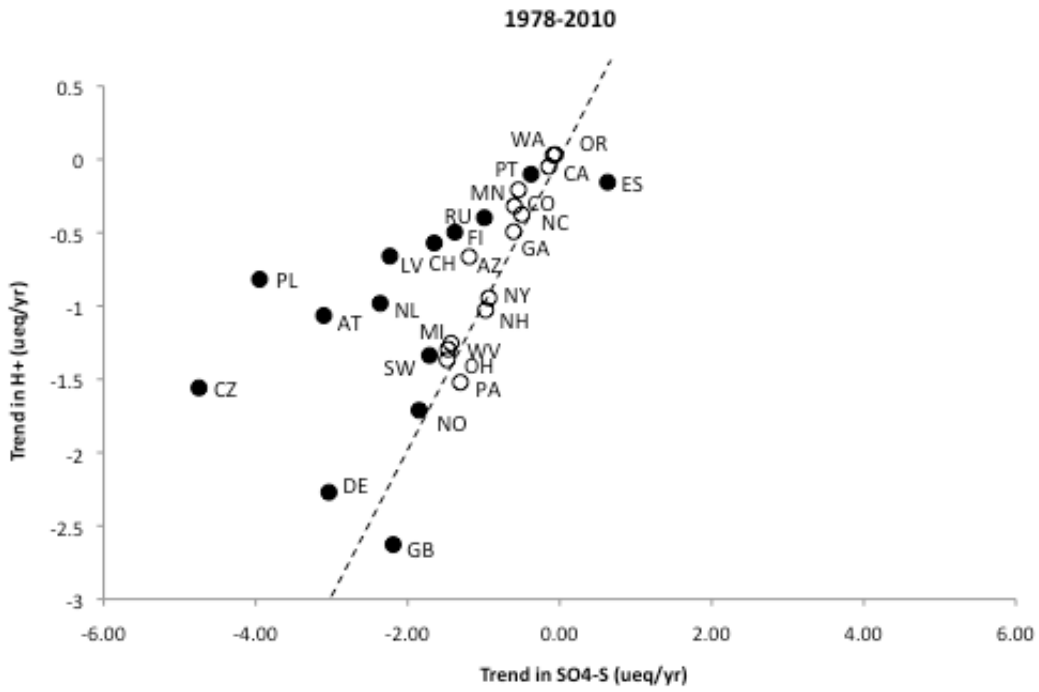


Fig. 6b.

Fig. 6 (b)

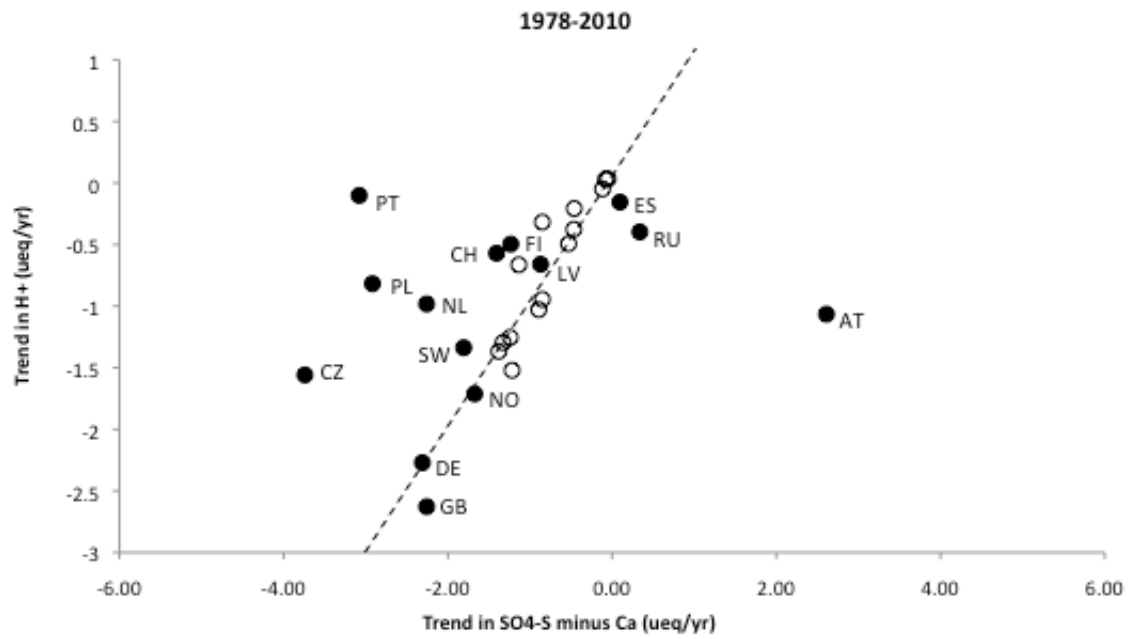


Fig. 6c.

Fig. 6 (c)

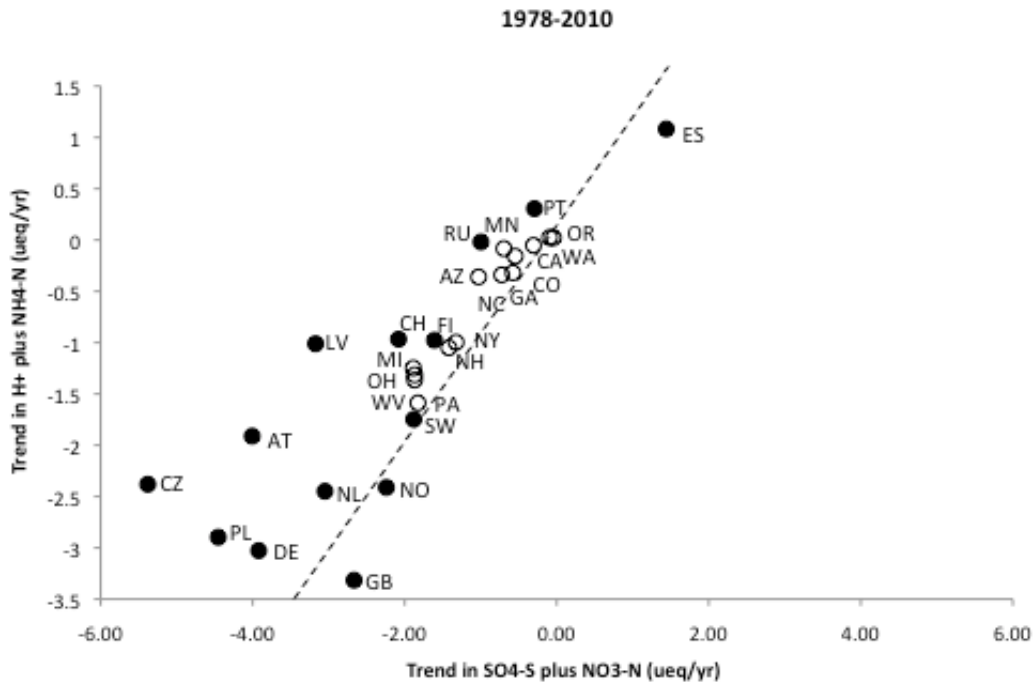


Fig. 7abc.

Fig. 7 (abc)

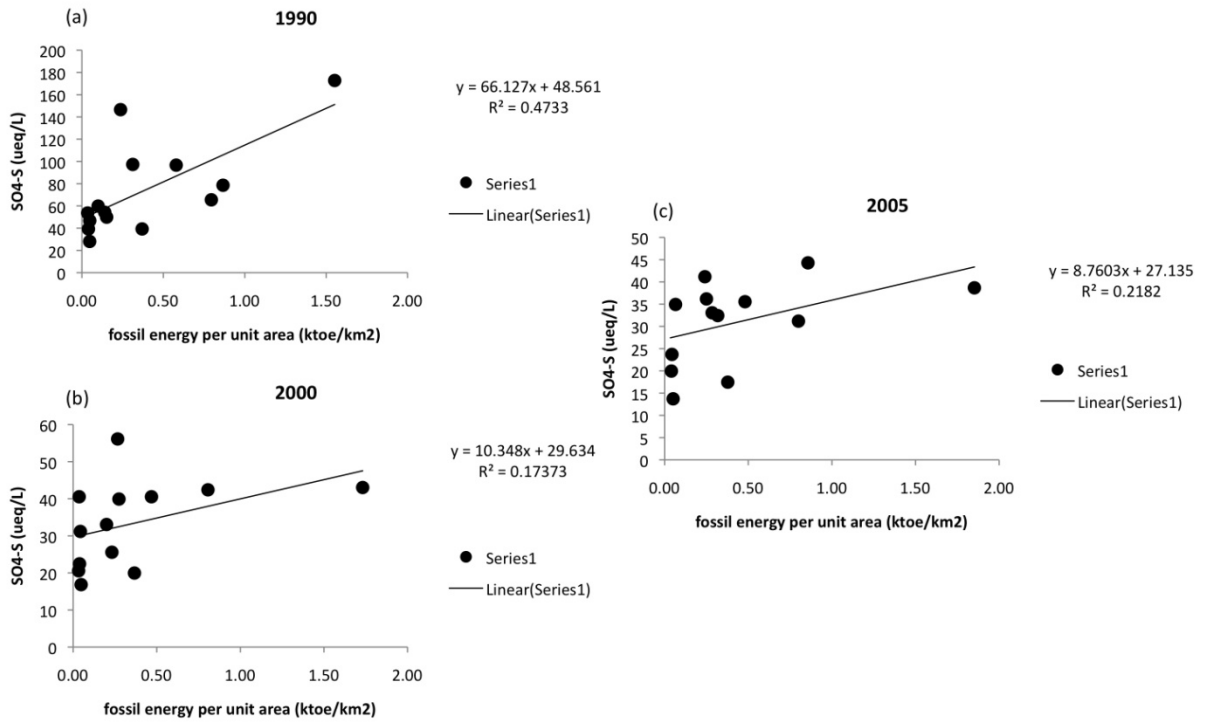


Fig. 7d.

Fig. 7 (d)

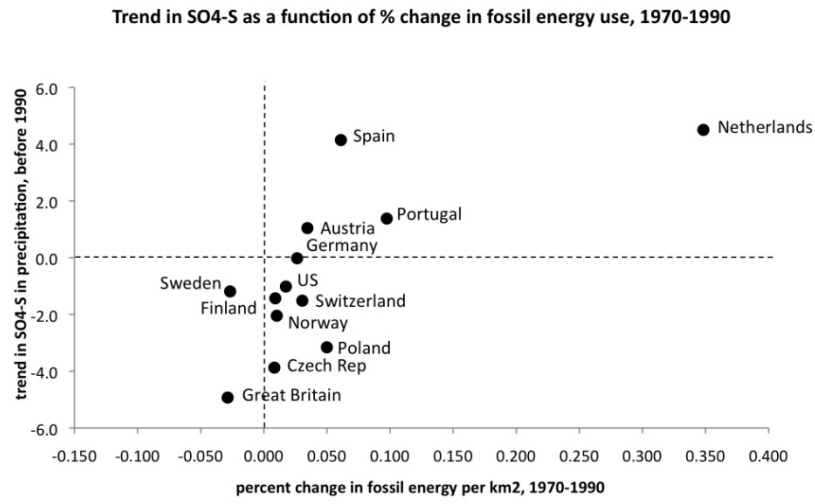


Fig. 7e.

Fig. 7 (e)

