# Long-term Trends in Aerosol and Precipitation Composition over the Western North Atlantic Ocean at Bermuda (ACP-2014-131-Revised)

William C. Keene[1*], Jennie L. Moody[1], James N. Galloway[1], Joseph M. Prospero[2], Owen R. Cooper[3], Sabine Eckhardt[4], and John R. Maben[1]

[1]Department of Environmental Sciences, Clark Hall, University of Virginia, Charlottesville, VA, 22904-4123, USA

[2]Division of Marine and Atmospheric Chemistry, University of Miami, 4600 Rickenbacker Causeway, Miami, FL, 33149-1098, USA

[3]Cooperative Institute for Research in Environmental Sciences (CIRES), University of Colorado and NOAA Earth Systems Research Laboratory, Boulder, CO, 80305, USA

[4]Norwegian Institute for Air Research, Kjeller, Norway

*Corresponding author (e-mail: wck@virginia.edu)

Abstract

Since the 1980s, emissions of $SO_2$ and $NO_x$ ($NO + NO_2$) from anthropogenic sources in the United States (US), Canada, and Europe have decreased significantly suggesting that the export of oxidized S and N compounds from surrounding continents to the atmosphere overlying North Atlantic Ocean (NAO) has also decreased. The chemical compositions of aerosols and precipitation sampled daily on Bermuda (32.27 N, 64.87 W) from 1989 to 1997 and from 2006 to 2009 were evaluated to quantify the magnitudes, significance, and implications of associated tends in atmospheric composition. The chemical data were stratified based on FLEXPART retroplumes into four discrete transport regimes: Westerly flow from the eastern North America (NEUS/SEUS); easterly trade-wind flow from northern Africa and the subtropical NAO (Africa); long, open-ocean, anticyclonic flow around the Bermuda High (Oceanic); and transitional flow from the relatively clean open ocean to the polluted eastern North America (North). Based on all data, annual average concentrations of non-sea-salt (nss) $SO_4^{2-}$ associated with aerosols and annual volume-weighted-average (VWA) concentrations in precipitation decreased significantly (by 22% and 49%, respectively) whereas annual VWA concentrations of $NH_4^+$ in precipitation increased significantly (by 70%). Corresponding trends in aerosol and precipitation $NO_3^-$ and of aerosol $NH_4^+$ were insignificant. Nss $SO_4^{2-}$ in precipitation under NEUS/SEUS and Oceanic flow decreased significantly (61% each) whereas corresponding trends in particulate nss $SO_4^{2-}$ under both flow regimes were insignificant. Trends in precipitation composition were driven in part by decreasing emissions of $SO_2$ over upwind continents and associated decreases in anthropogenic contributions to nss $SO_4^{2-}$ concentrations. Under NEUS/SEUS and Oceanic flow, the ratio of anthropogenic to biogenic contributions to nss $SO_4^{2-}$ in the column scavenged by precipitation were relatively greater than those in near surface aerosol, which implies that, for these flow regimes, precipitation is a better indicator of overall anthropogenic impacts on the lower troposphere. Particulate nss $SO_4^{2-}$ under African flow also decreased significantly (34%) whereas the corresponding decrease in nss $SO_4^{2-}$ associated with precipitation was insignificant. We infer that these trends were driven in part by reductions in the emissions and transport of oxidized S compounds from Europe. The lack of significant trends in $NO_3^-$ associated with aerosols and precipitation under NEUS/SEUS flow is notable in light of the large decrease (37%) in $NO_x$ emissions in the US and Canada over the period of record. Rapid chemical processing of oxidized N in marine air contributed to this lack of correspondence. Decreasing ratios of nss $SO_4^{2-}$ to $NH_4^+$ and the significant decreasing trend in precipitation acidity (37%) indicate that the total amount of acidity in the multiphase gas-aerosol system in the western NAO troposphere decreased over the period of record. Decreasing aerosol acidities would have shifted the phase partitioning of total $NH_3$ ($NH_3$ + particulate $NH_4^+$) towards the gas phase thereby decreasing the atmospheric lifetime of total $NH_3$ against wet plus dry deposition. The trend of increasing $NH_4^+$ in precipitation at Bermuda over the period of record suggests that $NH_3$ emissions from surrounding continents also increased. Decreasing particulate nss $SO_4^{2-}$ in near-surface air under NEUS/SEUS flow over the period of record implies that the corresponding shortwave scattering and absorption by nss S and associated aerosols constituents also decreased. These changes in radiative transfer suggest a lower limit for net warming over the period in the range of 0.1 to 0.3 W $m^{-2}$.

## 1. Introduction

It has been recognized for many years that material emitted to the atmosphere from continental sources can be transported long distances over adjacent oceans. For example, reports of crustal aerosol transported from northern Africa over the open North Atlantic Ocean (NAO) have been published in the scientific literature since the late 1700s (e.g., Dobson, 1781; Darwin, 1846). More recently, trace elements and reaction products from S and N species emitted by anthropogenic combustion and industrial sources were detected in atmospheric aerosols and precipitation over the NAO (e.g., Zoller et al., 1973; Jickells et al., 1982; Chen and Duce, 1983). Subsequent, studies have attempted to quantitatively differentiate relative contributions from major source types (continental versus marine; anthropogenic versus biogenic versus crustal) and major source regions based on analysis of elemental and molecular tracers (e.g., Arimoto et al., 1995; Savioe et al., 2002), radionuclides (e.g., Arimoto et al., 1999), isotopic composition (e.g, Turekian et al., 2001, 2003; Hastings et al., 2003; Lin et al., 2012), air-mass transport history (e.g., Moody and Galloway, 1988; Galloway et al., 1989; Moody et al., 1995, 2014), and satellite remote sensing (e.g., Zhao et al., 2008; Zhang and Reid, 2010; Hsu et al., 2012; Prospero et al., 2012). These and other studies indicate that the transport of anthropogenic emissions and reaction products from North America is the dominant source of pollutants associated with aerosols and precipitation over the western NAO at Bermuda. However, anthropogenic emissions from surrounding continents have changed significantly over the past quarter century suggesting that relative impacts of anthropogenic sources to air quality over the western NAO have also changed.

Implementation of the Clean Air Act and associated amendments in the United States (US) and similar legislation in Europe in the late 1980s and early 1990s led to substantial reductions in emissions of $SO_2$ and $NO_x$ to the atmosphere surrounding the North Atlantic basin (e.g., Vestreng, 2007; Hand et al., 2012). For example, emissions inventories prepared by the US Environmental Protection Agency (EPA, 2013) indicate that, between 1980 and 2012, total emissions of $SO_2$ and $NO_x$ in the US decreased by factors of 80% and 50%, respectively. In contrast, reported emissions of $NH_3$ in the US between 1990 (the earliest year available) and 2012 differed by less than 1% (EPA, 2013). Thus, the relative mixture of acids (from $SO_2$ and $NO_x$ oxidation) and bases in the planetary boundary layer (PBL) over the US and, presumably, associated pH-dependent chemical processes, also evolved temporally over this period. Reductions in $SO_2$ and $NO_x$ emissions led to corresponding decreases in annual average $SO_2$ and $NO_x$ mixing ratios in ambient air over the US during the same period (factors of 78% and 56%, respectively) (EPA, 2013). Concentrations of particulate-phase reaction products from the oxidation of $SO_2$ and $NO_x$ as well as aerosol optical depth (AOD) also decreased and visibility improved. For example, between 2000 (the earliest year available) and 2012, average annual concentrations of PM2.5 mass in near-surface air over the US decreased by 33% (EPA, 2013), between 2000 and 2010, particulate $SO_4^{2-}$ concentrations in rural areas of the US decreased by 27% (Hand et al., 2012), and, between 1980 and 2006, simulated AOD over the US decreased by 38% (Streets et al., 2009). Reductions in emissions have also led to large decreases in the atmospheric deposition of $SO_4^{2-}$, $NO_3^-$ and $H^+$ and the associated recovery of some degraded watersheds in the eastern US (Kahl et al., 2004; Webb et al., 2004; Leibensperger et al., 2012).

The above trends for the US suggest that the physicochemical properties of the western NAO atmosphere have also changed significantly over the past quarter century analogous to the sharp decreases in lead over the NAO that followed phase out of leaded gasoline in the US (Shen and

Boyle, 1987). Although not significant, Zhang and Reid (2010) reported a decreasing trend in AOD over the western NAO between 2000 and 2009. During the same period $SO_2$ and $NO_x$ emissions in the US decreased by 49% and 31%, respectively, and simulated AOD over the continental US also decreased (Streets, et al., 2009). Based on satellite observations of AOD and the chemical composition of near-surface aerosols, Moody et al (2014) estimate that, under transport from the northeastern US during the period 2006 to 2009, pollutant aerosol accounted for direct radiative cooling at Bermuda of 1.0 to 2.2 W $m^{-2}$. However, potential changes in AOD resulting from emissions reductions in the US were not evaluated.

In this paper, we investigate long-term trends in the chemical composition of aerosols and precipitation over the western NAO at Bermuda with a focus on evaluating impacts of emissions reductions and influences of different source regions. This work is based on measurements between 1989 and 1997 under the auspices of the Atmosphere Ocean Chemistry Experiment (AEROCE) and comparable measurements between 2006 and 2009 at the same location.

## 2. Methods

### 2.1. Sampling Site, Periods, and Protocols

From June 1988 through July 1998, aerosols in sectored (on-shore) flow at the Tudor Hill Atmospheric Observatory (THAO) on Bermuda (32.27 N, 64.87 W) were sampled daily for chemical characterization from the top of a 23-m scaffolding tower situated on a steep slope about 25 m above sea level. Samples were collected in bulk at a nominal flow rate of 1.0 $m^3$ $min^{-1}$ on Whatman 41 filters (20.3 x 25.4 cm) as part of AEROCE (Galloway et al., 1993; Savoie et al., 2002). Data were blank corrected based on analysis of paired bulk-filter cassettes deployed periodically in parallel with samples but through which no air was pulled.

From July 2006 through June 2009, dichotomous aerosol (nominal super- and sub-μm-diameter size fractions) was sampled daily at a rate of 0.1 $m^3$ $min^{-1}$ with a custom-designed and fabricated MSP model 130 high-flow cascade impactor configured with Liu-Pui type omnidirectional inlet (Liu et al., 1983). Relative to MSP's Micro-Orifice Uniform Deposit Impactor (MOUDI) (Marple et al., 1991) that is in more widespread use by the research community, these hi-flow impactors yield greater signal per unit deployment time while segregating aerosol size fractions using similar nozzle technology. Impactors were deployed at the top of the THAO tower (Moody et al., 2014). The calculated inlet passing efficiency for 20-μm-diameter particles was 95% and the 50% aerodynamic cut between the two size factions was 0.8-μm ambient diameter. Impactors were configured with quartz-fiber (Pallflex 2500 QAT-UP) substrates (75-mm diameter) and back filters (90-mm diameter). Dichotomous data were blank corrected based on analysis of impactor substrates and back filters through which air was briefly pulled (~15 sec). Between 2006 and 2009, a blank impactor was exposed and processed approximately once every two weeks.

With the exception of the differences noted above, aerosol sampling and handling procedures prior to analysis during both periods were virtually identical. Sampling was controlled by sensors that activated pumps only during periods of no precipitation when surface winds were off the ocean sector at speeds greater than 1 m $sec^{-1}$. Air volumes were measured with sharp-edged

flow tubes and normalized to standard temperature and pressure ($0^o$ C and 1 atm). Bulk cassettes and impactors were cleaned with 18 MΩ $cm^{-1}$ deionized water (DIW), and dried, loaded, and unloaded in a Class 100 clean bench mounted in a laboratory container at the base of the tower. After recovery, exposed sample and blank filters and substrates were folded in half, sealed in clean polyethylene bags, and stored (and shipped) frozen prior to analysis. Samples and corresponding blanks during each period were processed and analyzed using identical analytical procedures.

From July 1988 through April 1997 and from July 2006 through June 2009, wet-only precipitation in unsectored air was sampled daily from the top of the THAO tower in precleaned 13.2 L polyethylene buckets mounted in an automated collector (Galloway et al., 1993). Precipitation amount was measured in parallel with both bulk and recording rain gauges; precipitation amounts reported herein correspond to those measured with the bulk gauge. After recovery, sample aliquots (250 mL or less for low volume events) were transferred to precleaned polyethylene bottles, sterilized on site via addition of 500 μL $CHCl_3$ to prevent microbial activity (Keene et al., 1983; Herlihy et al., 1987), and stored refrigerated prior to analysis. During both periods, precipitation was sampled and processed prior to chemical analysis using identical procedures.

## 2.2. Sample Analysis

Aerosol sampled from 1988 to 1998 was analyzed at the University of Miami (UM) for $SO_4^{2-}$, $NO_3^-$, and $NH_4^+$ by suppressed ion chromatography (IC), and for $Na^+$ by flame atomic absorption spectroscopy (AA) (Galloway et al., 1993; Savoie et al., 2002). From 1988 to 1996, particulate $CH_3SO_3^-$ was also measured at UM by IC. Aerosols sampled from 2006 to 2009 were analyzed at the University of Virginia (UVA) by IC for $CH_3COO^-$, $HCOO^-$, $(COO)_2^{2-}$, $CH_3SO_3^-$, $SO_4^{2-}$, $Cl^-$, $Br^-$, $NO_3^-$, $NH_4^+$, $Na^+$, $K^+$, $Mg^{2+}$, and $Ca^{2+}$ (Moody et al., 2014).

Precipitation sampled during both periods was analyzed for major ionic constituents at UVA. From 1988 to 1997, $H^+$ was measured by electrode and meter, anions ($CH_3COO^-$, $HCOO^-$, $CH_3SO_3^-$, $SO_4^{2-}$, $Cl^-$, $Br^-$, and $NO_3^-$) were measured by IC, $NH_4^+$ was measured by the automated indophenol blue technique, and base cations ($Na^+$, $K^+$, $Mg^{2+}$, and $Ca^{2+}$) were measured by AA (Galloway et al., 1993). From 2006 to 2009, $H^+$ was measured by electrode and meter and the other major ions (the same suite as indicated above for aerosols during this period) were measured by IC using procedures described by Moody et al. (2014).

## 2.3. Data Quality and Comparability

The quality of data for aerosols and precipitation sampled from 1988 to 1998 is described in detail by Galloway et al. (1993) and Savoie et al. (2002). During both the earlier and later sampling periods, data for aerosol samples that corresponded to in-sector times of less than 2.4 hours (10% of a day) exhibit low signal-to-noise and may not be representative; consequently, these results were excluded from the final quality-assured data set. In addition, five samples contained unusually high concentration of sea-salt constituents (30% to 380% higher than the sample with the next highest concentrations) and/or operator notes that suggest direct

contamination by rainwater or splash; data for these samples were also excluded from the final quality-assured data set.

Detection limits (DLs) for all analytes measured from 2006 to 2009 were estimated following Keene et al. (1989). Because in-sector sampling times for aerosols included in the data set varied from 10% to 100% of the corresponding deployment times, DLs for particulate-phase species varied among samples and, thus, were calculated individually for each analyte in each sample (Moody et al., 2014). Analytical performance was verified by intercomparison of the UVA laboratory with those at UM and the University of New Hampshire, among others; routine analysis of audit solutions from the National Institute of Standards and Technology, the World Meteorological Association, and the US Environmental Protection Agency; periodic analysis of standard additions to samples, and evaluation of ion balances and constituent ratios. These comparisons indicate that the ionic data generated by both UVA and UM are unbiased.

Based on their thermodynamic properties (Henry's Law and dissociation constants), the equilibrium phase partitioning of $HNO_3$ and $NH_3$ varies as a function of aerosol solution pH; $HNO_3$ partitions preferentially with the less acidic super-um size fractions of marine aerosol whereas $NH_3$ partitions preferentially with the more acidic sub-um size fractions (e.g., Moody et al., 2014). In addition, larger aerosol size fractions in ambient air may be undersaturated with respect to the gas phase because (1) their surface-to-volume ratios are relatively low and thus equilibration times are relatively slow and (2) they exhibit relatively short atmospheric lifetimes against deposition (e.g., Keene et al., 2004). When chemically distinct marine aerosols are sampled in bulk (or in relatively coarse size fractions) the pH of the mixed sample may diverge from those for the size fractions with which most $NO_3^-$ and $NH_4^+$ was associated in ambient air and thereby drive artifact phase changes (e.g., Keene et al., 1990). Explicit evaluation of the magnitude of such artifacts is beyond the scope of this study but, because different sampling methodologies were employed during the earlier and later periods, artifacts of this nature could influence temporal trends based on measured particulate-phase concentrations of these analytes. We return to this point below. Because $H_2SO_4$ is highly soluble over the reported range in aerosol pH, particulate $SO_4^{2-}$ is not subject to sampling artifacts of this nature.

## 2.4. Calculations

Contributions to measured $SO_4^{2-}$ from sea-salt and non-sea-salt sources were differentiated following (Keene et al., 1986) for all samples for which the measured concentrations of total $SO_4^{2-}$ and the sea-salt reference species were above detection limits (DL). Between 1988 and 1998, nss $SO_4^{2-}$ associated with aerosols was calculated using $Na^+$ as the sea-salt references species and the mass ratio of $SO_4^{2-}$ to $Na^+$ in surface seawater reported by Millero and Sohn (1992) (0.2516). As indicated above, between 2006 and 2009, super- and sub-μm aerosol size fractions were sampled on 75-mm and 90-mm diameter quartz-fiber substrates and filters, respectively. Background concentrations of the two mostly commonly used sea-salt reference species ($Na^+$ and $Mg^{2+}$) in extracts of blanks for the two filter sizes differed such that $Na^+$ offered greater resolution in calculating nss $SO_4^{2-}$ associated with the super-μm-diameter aerosol size fraction whereas $Mg^{2+}$ offered greater resolution for nss $SO_4^{2-}$ associated with the sub-μm-diameter size fraction. Super- and sub-μm-diameter nss $SO_4^{2-}$ was calculated accordingly based on the mass ratios of $SO_4^{2-}$ to $Na^+$ and $SO_4^{2-}$ to $Mg^{2+}$ in surface seawater reported by Wilson

(1975), (0.2518 and 2.102, respectively). Minor differences between the seawater compositions reported by Millero and Sohn (1992) and Wilson (1975) (less than 0.1%) used in the above calculations were an insignificant source of bias in resulting nss concentrations. Over the entire period of record, nss $SO_4^{2-}$ in precipitation was calculated based on $Na^+$ as the reference species and the seawater composition reported by Wilson (1975).

Concentrations of ionic species associated with super- and sub-μm-diameter aerosol size fractions measured during 2006 to 2009 were summed (Moody et al., 2014) for comparison with the chemical composition of aerosol sampled in bulk during the earlier period of record. To evaluate temporal trends over the entire period of record, data were binned into sample years based on the midpoint of the each daily sampling interval. Aerosol constituents are reported as annual average concentrations and precipitation constituents are reported as VWA concentrations. FLEXPART retroplumes (see below) were not available to characterize transport for the samples collected prior to 1 January 1989. Consequently, from 1989 through 1997, sample years were defined as 1 January through 31 December and temporal trends were interpreted based on the corresponding mid-year date of 1 July. Because the later 3-year period of record started in mid-2006 and ended in mid-2009, sample years were defined as 1 July through 30 June and interpreted based on the mid-year date of 1 January. This approach yielded three full (12-month) sample years over the period of record. If based on calendar year, the last six months of 2006 and the first six months of 2009 would have been excluded yielding only two years for the analysis.

## 2.5. Atmospheric Transport

The particle dispersion model FLEXPART (Stohl et al., 1998, 2005) was run in backward mode (Stohl et al., 2003; Seibert and Frank, 2004) to generate the column residence times and footprint residence plots for source regions associated with the sampled air parcels. FLEXPART was driven with ECMWF analyses of 0.36-degree resolution and accounts for turbulence and deep convection in addition to the transport by grid-resolved winds. At 15 UTC (the approximate midpoint of the deployment times for aerosol and precipitation samplers), 40,000 particles were released from the location of the measurement site and followed backward in time for 10 days Primary flow regimes were characterized based on proportional footprint residence times within four prescribed source regions from which air was transported to Bermuda. See Moody et al., (2014) for detailed explanation of the procedure employed to identify primary air-mass source regions for aerosols sampled at Bermuda during 2006 through 2009 and examples of retroplumes for each flow regime. An identical approach was applied to characterize source regions for aerosols sampled during 1989 to 1997 and for precipitation sampled during both periods. Wind fields were not available for the first six months of 1990. Because retroplumes could not be calculated for that period, annual statistics for 1990 were not included in the evaluation of trends associated with air transported from different source regions.

Moody et al. (2014) identified two distinct flow regimes that transported aerosols from eastern North America to Bermuda. One was associated with predominant flow from the northeastern United States (NEUS) and southern Canada and the other with predominant flow from southeastern US (SEUS) and the Gulf of Mexico. To evaluate trends associated with the combined flow off northern and southern regions of eastern North America, the NEUS and

SEUS flow regimes were merged for this analysis into a single group (referred to as 'NEUS/SEUS'). Transport from northern Africa and the tropical NAO region (referred to as 'Africa') was associated with trade-wind flow along the southern portion of the Bermuda High (BH). The 'Oceanic' flow regime was generally associated with long trajectories over the open ocean under anticyclonic flow around the BH. The 'North' transport regime represented transitional flow from the relatively clean open ocean to the polluted eastern North America. Data evaluated herein were classified accordingly; the total numbers of samples and corresponding mean precipitation amounts in the final data base partitioned by flow regime and year are summarized in Table 1. The relatively fewer numbers of aerosol samples for the period 2006 to 2009 reflects the fact that 1) dichotomous rather than bulk aerosol was sampled during the later period and thus the super- and sub-μm-diameter size fractions of each sample were segregated and analyzed separately and 2) sampling rates through the high-flow impactor were a factor of 10 lower that those through the hi-volume bulk sampler. Although analytical resolution per unit analyte concentration in extract solutions was higher during the latter period, the absolute amount of analyte present in each size fraction was lower relative to bulk aerosol during the earlier part of the record. Consequently, relatively fewer aerosol constituents were present in samples at concentrations above DLs during 2006 to 2009.

## 2.6. Statistical Evaluations

The statistical package SPSS was used to evaluate temporal trends in the data using two complimentary approaches. (1) Trends were characterized based on slopes of standard linear regressions (SLRs) for annual average concentrations of aerosol constituents versus time and for annual VWA concentrations of precipitation constituents versus time. (2) Temporal trends in annual mean (for aerosols) and annual VWA (for precipitation) constituent concentrations were also characterized based on slopes calculated using the bootstrapping method applied to all individual daily data (Freedman, 1981). The significance of each bootstrap slope was evaluated using a two-tailed test based on 1000 random samples of the corresponding data subset. Relative to SLRs, this method provides a more robust evaluation of significance in trends. For smaller data sets, the approach resulted in redundant subsampling. In these cases the actual significance thresholds may have deviated somewhat from the calculated values. However, sensitivity evaluations employing smaller numbers of random samples yielded virtually identical results suggesting that any such deviations were small to negligible. Interannual variability in mean or VWA constituent concentrations is the only source of variance in the SLRs whereas seasonal variability contributes significantly to overall variance based on the bootstrap method. Consequently, substantially less overall variance in long-term trends is explained by bootstrapping. Because this analysis focuses on long-term trends, reported variances correspond to those for SLRs.

In addition to the calculations summarized above, trends in annual median aerosol and precipitation concentrations and in per-event wet-deposition fluxes were also quantified for selected data subsets to evaluate the sensitivity of results to the underlying sample statistics used in the analysis. Results were reasonably consistent with those based on annual mean concentrations for aerosols and annual VWA concentrations for precipitation. We interpret results based on these latter more widely used conventions for reporting and evaluating

concentrations of aerosol and precipitation constituents thereby facilitating direct comparison with previously published results.

## 3. Results and Discussion

### 3.1. Temporal Trends in the Chemical Composition of Aerosols and Precipitation

Temporal trends in annual average concentrations of particulate nss $SO_4^{2-}$, $NO_3^-$, and $NH_4^+$ and corresponding trends in annual VWA concentrations in precipitation based on all quality-assured data over the period of record at Bermuda are depicted in Figure 1. Nss $SO_4^{2-}$ concentrations for both aerosols and precipitation decreased significantly but the percentage decrease in VWA concentrations based on the SLR for precipitation (49%) was greater than the corresponding decrease in annual mean concentrations for aerosols (24%, Table 2). In contrast, the VWA concentration of $NH_4^+$ in precipitation increased significantly (70%) over the period of record whereas the trend in particulate $NH_4^+$ was insignificant (Table 2). Concentrations of $NO_3^-$ associated with aerosols and precipitation also did not vary significantly (Table 2). These results suggest long-term changes in atmospheric composition and also indicate that relative trends in the composition of precipitation and near-surface aerosols diverge. However, substantial interannual variability is evident for all species in both phases (Fig. 1a,b) and the corresponding linear regressions explain less than 50% of the variance over the period of record.

### 3.2. Temporal Trends Based on FLEXPART Flow Patterns

Year-to-year variability in frequencies of transport from different source regions is one of the major factors that drives interannual variability in atmospheric composition at a given location. Such influences can be minimized by evaluating trends in concentrations as a function of transport regime. As was the case for the data subset corresponding to aerosols sampled from 2006 to 2009 (Moody et al., 2014), segregation by source region differentiated analyte concentrations into chemically distinct subgroups. For most years, the upper limits for mean concentrations of aerosol and precipitation constituents were associated with polluted NEUS/SEUS flow from North America whereas the lower limits were associated with background Oceanic flow around the BH (Fig. 2). Analytes associated with the Africa and North flow regimes generally fell within the range bounded by the other two regimes. However, numbers of samples per year varied substantially among flow regimes (Table 1). The relatively small numbers of samples collected under Oceanic and North flow in particular constrain the power of statistical approaches for evaluating associated temporal trends and thus caution is warranted in their interpretation.

Because regional transport varies seasonally, segregating data by source region also segregated to some extent by season. For example, efficient transport of North American emissions over the western NAO is typically associated with frontal passages, which are most frequent during winter and spring, whereas transport from Northern Africa to the western NAO in association with the easterly trade wind regime is most frequent during summer. Factors other than precursor emissions within and the frequencies of flow from source regions also contribute to seasonal variability in aerosol and precipitation composition among flow regimes. Relative to colder months, higher ultraviolet radiation and temperatures during warmer months sustain faster

rates of precursor oxidation and secondary aerosol production. The temperature-dependent emissions of $NH_3$ contribute to seasonal variability in the nucleation and growth of new particles. Seasonal variability in precipitation fields and in the temperature-dependent partitioning of semi-volatile species between the gas and particulate phases also drive seasonal variability in atmospheric lifetimes and associated transport and deposition fields. Although these and other processes contribute to overall variability in aerosol and precipitation composition as a function of source region, our data lack adequate resolution to quantitatively differentiate relative influences. See Moody et al. (2014) for a detailed evaluation of season variability in the sources and composition of aerosols at Bermuda between 2006 and 2009.

3.1.1. nss $SO_4^{2-}$

Based on slopes for SLRs fit to annual average concentrations, VWA nss $SO_4^{2-}$ in precipitation associated with the NEUS/SEUS flow regime decreased significantly (61%) over the period of record whereas the corresponding trend in particulate nss $SO_4^{2-}$ was marginally insignificant ($p$ = 0.12, Figs 2a,b, Table 2). The absence of a significant trend in particulate nss $SO_4^{2-}$ for the NEUS/SEUS flow was driven in part by the missing data for 1990. Based on all data (Fig. 1a), 1990 exhibited the highest mean concentration over the period and most samples during each year were associated with the NEUS/SEUS regime (Table 1). Between 1989 and 2009, $SO_2$ emitted over the US and Canada decreased by 60% (Fig. 3). Although the overall decrease in VWA nss $SO_4^{2-}$ in precipitation based on the SLR was similar to that for $SO_2$ emissions over the US and Canada during the period of record, the temporal patterns within the period of record were distinct. Most of the decrease in VWA nss $SO_4^{2}$ was associated with a significant negative trend between 1991 and 1996 (SLR slope = -0.62, $r^2$ = 0.84, Fig. 2b). Based on the SLR for 1991 through 1996, annual VWA nss $SO_4^{2-}$ during the period decreased by 51% whereas, over the same period, $SO_2$ emissions in the US and Canada decreased by only 17% (Fig. 3). It is evident from the above that (1) the declines in nss $SO_4^{2-}$associated with both near-surface aerosols and precipitation under NEUS/SEUS flow were not directly proportional to the decline in $SO_2$ emissions over the US and Canada and (2) factors other than $SO_2$ emissions over the North American source region influenced trends in nss $SO_4^{2-}$ associated with near-surface aerosols and precipitation under NEUS/SEUS flow differentially.

Significant amounts of nss $SO_4^{2-}$ associated with aerosols and precipitation at Bermuda originate from the atmospheric oxidation of dimethylsulfide ($(CH_3)_2S$) produced in the surface ocean by marine biota and subsequently emitted to the atmosphere (Galloway et al., 1989; Savoie et al., 2002; Moody et al., 2014). Potential variability in biogenic contributions may have contributed to the differences in trends noted above. To evaluate potential influences of biogenic S, we employed the mass ratio of particulate nss $SO_4^{2-}$ to $CH_3SO_3^-$ yields from $(CH_3)_2S$ oxidation estimated from measurements at Bermuda (18.8±2.2, Savoie et al., 2002) to differentiate relative contributions from marine biogenic and anthropogenic sources to annual average concentrations of particulate nss $SO_4^{2-}$ associated with NEUS/SEUS flow (Fig. 4a). Briefly, in mass units, anthropogenic nss $SO_4^{2-}$ was estimated from total nss $SO_4^{2-}$ minus the product $CH_3SO_3^-$ * 18.8. Corresponding trends in annual VWA nss $SO_4^{2-}$ in precipitation were calculated (Fig. 4b) based on the assumption that the same product yields apply to precipitation. Trends in $CH_3SO_3^-$ (and thus biogenic contributions) for both aerosols and precipitation were insignificant, which indicates that long-term temporal variability in nss $SO_4^{2-}$ associated with both aerosols and

precipitation was driven primarily by differential variability in anthropogenic contributions. These results also indicate that relative contributions of anthropogenic sources to VWA nss $SO_4^{2-}$ in precipitation at Bermuda have decreased more rapidly that those to mean nss $SO_4^{2-}$ associated with aerosols (Fig. 4). For example, based on the corresponding SLRs, percentage contributions of anthropogenic sources to nss $SO_4^{2-}$ in precipitation and aerosols under NEUS/SEUS flow were roughly similar during the first sample year centered on 1 July 1989 (73% and 72%, respectively) whereas they diverge to a greater degree by the final sample year centered on 1 January 2009 (41% and 68%, respectively). We return to this issue below.

VWA nss $SO_4^{2-}$ associated with the Oceanic flow regime decreased significantly whereas the corresponding trend in particulate nss $SO_4^{2-}$ was insignificant (Fig. 2a,b, Table 2). Available evidence suggests that virtually all particulate nss $SO_4^{2-}$ in near-surface air sampled under Oceanic flow at Bermuda between 2006 and 2009 originated from the oxidation of $(CH_3)_2S$ (Moody et al., 2014). Corresponding trends in $CH_3SO_3^-$ associated with both aerosols and precipitation sampled under Oceanic flow over the entire period of record were insignificant. However, the relatively small numbers of observations per year (Table 1) coupled with seasonal variability in $CH_3SO_3^-$ concentrations (Moody et al., 2014) constrains resolution in explicitly evaluating biogenic versus anthropogenic contributions to total nss $SO_4^{2-}$ for this regime based on product yields as was done for the NEUS/SEUS regime. However, the similarities in annual mean particulate-phase nss $SO_4^{2-}$ under Oceanic flow during both the earlier and later periods of record (as reflected in the corresponding lack of a significant trend) indicates that the background particulate nss $SO_4^{2-}$ from biogenic sources in near-surface aerosol remained fairly constant over this 20-year period. In contrast, VWA nss $SO_4^{2-}$ in precipitation sampled under the same flow regime exhibited significant decreasing concentrations. Most nss $SO_4^{2-}$ in precipitation originates from the aqueous-phase oxidation of $SO_2$ in cloud droplets and scavenging of particulate nss $SO_4^{2-}$ from the air column (e.g., Mari et al., 2000; von Glasow et al., 2002) whereas aerosols evaluated herein were sampled near the surface. Our results suggest the possibility that the transport of pollutant S emitted from surrounding continents sustained relatively higher concentrations of oxidized S in aged marine air aloft, which contributed significantly to nss $SO_4^{2-}$ incorporated into precipitation but not into near-surface aerosols under Oceanic flow. As anthropogenic emissions from surrounding continents decreased over the period of record, contributions of pollutant S to background concentrations in aged marine air aloft over the NAO would have also decreased thereby contributing to the observed decline (61%) in VWA nss $SO_4^{2-}$ in precipitation sampled under Oceanic flow (Fig. 2b, Table 2).

The larger decrease in VWA nss $SO_4^{2-}$ associated with precipitation relative to aerosols in NEUS/SEUS flow discussed above would be consistent with our interpretation of trends for the Oceanic regime. Air masses transported off eastern North America over the western NAO may rise up over and become decoupled from the marine boundary layer (MBL) (Neuman et al., 2006) whereas most biogenic $(CH_3)_2S$ emitted from the ocean surface is oxidized within the MBL (e.g., Savoie et al., 2002). Most $SO_2$ in the MBL is oxidized to particulate $H_2SO_4$ via aqueous-phase pathways involving super-μm marine aerosols that have short lifetimes against deposition and cloud droplets (e.g., Keene et al., 1998; von Glasow et al., 2002). In addition, both $SO_2$ and sub-μm particulate nss $SO_4^{2-}$ in the MBL are depleted via dry deposition to the surface ocean. Consequently, oxidized S above the western NAO MBL, which available evidence suggests is primarily anthropogenic, should exhibit longer atmospheric lifetimes

against removal relative to that within the MBL, which includes most of the biogenic component. We hypothesize that the differential vertical distributions and associated atmospheric lifetimes of oxidized S from anthropogenic versus biogenic sources coupled with reductions in anthropogenic emissions contributed to relatively greater proportionate decreases in anthropogenic contributions to nss $SO_4^{2-}$ in precipitation versus near-surface aerosols over the period of record. Corresponding trends in nss $SO_4^{2-}$ associated with both aerosols and precipitation sampled under North flow were insignificant (Fig. 2a,b, Table 2) but the relatively small numbers of observations (Table 1) constrains resolution and, thus, caution is warranted in interpreting these results.

Particulate nss $SO_4^{2-}$ associated with the Africa flow regime decreased significantly (34%) over the period of record (Fig. 2a, Table 2). Based on the SLR, corresponding VWA nss $SO_4^{2-}$ concentrations in precipitation under Africa flow generally decreased, but unlike aerosols, this trend was not significant (Fig. 2b, Table 2). As was the case for the NEUS/SEUS regime, the temporal trends in biogenic nss $SO_4^{2-}$ (inferred from $CH_3SO_3^-$ as described above) were statistically indistinguishable from 0.0 for both aerosols (SLR slope = -0.007 nmol $m^{-3}$ $yr^{-1}$) and precipitation (SLR slope = -0.006 μmol $L^{-1}$ $yr^{-1}$), which implies that reductions in anthropogenic contributions drove the decreasing trends in nss $SO_4^{2-}$. We hypothesize that large reductions in $SO_2$ emissions over Europe (Vestreng et al., 2007) coupled with transport over the subtropical NAO in association with the easterly trade winds (e.g., Savoie et al., 1989) contributed to the trend of decreasing particulate nss $SO_4^{2-}$ for the Africa regime. However, unlike the differences in trends under NEUS/SEUS flow discussed above, proportionate decreases in nss $SO_4^{2-}$ associated with aerosols and precipitation under Africa flow based on the SLR slopes (Fig. 2a,b) were of roughly similar magnitude. Several factors may have contributed to differences in temporal trends for aerosols versus precipitation based on available data for the two regimes. Anthropogenic contributions to nss $SO_4^{2-}$ under Africa flow were significantly less than those under NEUS/SEUS flow (Moody et al., 2014). Based on the SLR for total particulate nss $SO_4^{2-}$ under Africa flow (Fig. 2a, Table 2) and that for the corresponding anthropogenic component calculated as described above (not shown), anthropogenic contributions to particulate nss $SO_4^{2-}$ decreased from 46% to 19% between 1989 and 2008-09. Based on the SLRs, the corresponding decrease for precipitation was of roughly similar magnitude (40% to 8%). Relative to the NEUS/SEUS, the lower absolute contributions of anthropogenic S to an interannually variable background of biogenic S afforded less resolution in evaluating trends for the Africa regime. In addition, available observations under Africa flow were relatively less frequent (Table 1), which further constrained resolution. Relatively longer transport times to Bermuda from Europe and Africa versus North America as well as differences in associated atmospheric dynamics for the two flow regimes may have also contributed to differences in trends. For example, during transport over the ocean, losses of biogenic S via deposition to the surface are continually replaced via oxidation of marine-derived $(CH_3)_2S$ whereas losses of anthropogenic S are not. Consequently, vertical gradients in the relative abundance of oxidized S from anthropogenic versus biogenic sources and the corresponding differences in ratios of anthropogenic to biogenic S scavenged from the column by precipitation versus those for near-surface aerosols would be expected to decrease with distance from anthropogenic source regions. Finally, to the extent that interactions with mineral aerosol influence the atmospheric lifetime of oxidized S against deposition, long-term temporal variability in mineral aerosol under transport from Africa to the

western NAO (e.g., Evan et al., 2006) may have modulated the trend in associated particulate nss $SO_4^{2-}$ relative to that for the NEUS/SEUS regime.

3.1.2. $NO_3^-$

Under NEUS/SEUS flow, trends based on SLRs fit to $NO_3^-$ concentrations associated with both aerosols and precipitation over the entire period of record were insignificant (Fig. 2c,d; Table 2). In contrast, emissions of $NO_x$ over the US and Canada decreased by 37% during this period (Fig. 3). The reported increase in $NO_x$ emissions in the US between 2001 and 2002 reflects an artifact that resulted from a change in the method used to estimate road emissions (R. L. Dennis, US EPA, personnel communication, 2014). Like VWA nss $SO_4^{2-}$ in precipitation at Bermuda, the corresponding VWA $NO_3^-$ also decreased significantly between 1991 and 1996 (SLR slope = -0.50, $r^2 = 0.83$) but, unlike nss $SO_4^{2-}$, $NO_3^-$ concentrations in precipitation recovered during the latter period (2006 to 2009) to levels similar to those during the late 1980s and early1990s (Fig. 2d). In contrast, $NO_x$ emissions over the US and Canada decreased by only 1% between 1991 and 1996 (Fig. 3). Comparable decreases in particulate $NO_3^-$ between 1991 and 1996 were not evident (Fig. 2c). The annual average $NO_3^-$ concentrations associated with aerosols under the NEUS/SEUS regime were generally higher than those for other regimes whereas VWA concentrations for precipitation overlapped to a greater degree (Fig. 2c,d). Presumably these relatively higher concentrations reflect contributions from reaction products of pollutant $NO_x$ emitted over eastern North America. However, temporal trends in $NO_3^-$ associated with both near-surface aerosols and precipitation under NEUS/SEUS flow appear to be largely decoupled from those of upwind $NO_x$ emissions in the US. In addition, temporal variability in particulate $NO_3^-$ in near-surface aerosols was distinct from that for VWA $NO_3^-$ in precipitation. We speculate that the efficient oxidation of $NO_x$ to $HNO_3$ in marine air coupled with the subsequent partitioning of most $HNO_3$ with large, short-lived marine-aerosol (e.g., Russell et al., 2003; Fischer et al., 2006; Keene et al., 2009) tended to attenuate temporal variability in near-surface particulate $NO_3^-$ under a given flow regime relative to both upwind emissions of precursor $NO_x$ and particulate species such as nss $SO_4^{2-}$ and $NH_4^+$ that are associated primarily with longer-lived sub-um aerosol in marine air. The decreasing concentrations of primary marine aerosol with altitude and corresponding influences on $HNO_3$ phase partitioning may have also contributed to divergence in the temporal variability in near-surface particulate $NO_3^-$ relative to $NO_3^-$ scavenged from the column by precipitation. However, corresponding trends in mean particulate $Na^+$ and VWA $Na^+$ in precipitation at Bermuda (not shown) over the study period were not significant, which implies that interannual variability in production of marine aerosol did not directly influence tends in $NO_3^-$. It is unclear why temporal trends in $HNO_3$ and particulate $NO_3^-$ scavenged from the column by precipitation under NEUS/SEUS flow did not vary in response to corresponding decreases in emissions of precursor $NO_x$ over the upwind source region.

VWA $NO_3^-$ in precipitation associated with flow from the North increased significantly over the period of record (Fig. 2d, Table 2). All other trends in $NO_3^-$ concentrations for both aerosols and precipitation were insignificant at $p$ of 0.05.

3.1.3. $NH_4^+$

Temporal trends in $NH_4^+$ associated with both aerosols and precipitation under NEUS/SEUS flow were similar to those for $NO_3^-$; none were significant (Fig. 2e,f and Table 2). The lack of significant trends in $NH_4^+$ concentrations is consistent with expectations based on trends in reported $NH_3$ emissions over the US and Canada, which increased by only1% between 1990 and 2009 (Fig. 3). The reported decrease in $NH_3$ emissions in the US between 2000 and 2001 is an artifact associated with a change in the method used to estimate emissions (R. L. Dennis, US EPA, personnel communication, 2014). Like both nss $SO_4^{2-}$ and $NO_3^-$, VWA $NH_4^+$ concentrations in precipitation decreased significantly during the early period of record (1991-1996) (SLR slope = -0.19, $r^2 = 0.40$) and then recovered (Fig. 2f). In contrast, between 1991 and 1996, reported $NH_3$ emissions in the US and Canada increased by 9% (Fig. 3).

Like nss $SO_4^{2-}$, particulate $NH_4^+$ associated with the Africa regime decreased significantly over the study period. In contrast, VWA $NH_4^+$ in precipitation sampled under Africa flow increased significantly (Fig. 2e,f, Table 2). As discussed in more detail below, these opposite trends may be driven in part by decreases in the acidity of the multiphase system and associate shifts in gas-aerosol phase partition of $NH_3$. All other trends in $NH_4^+$ were insignificant.

## 3.2. Implications

It is evident from the above that, in many cases, interannual variability and long-term trends in mean nss $SO_4^{2-}$, $NO_3^-$, and $NH_4^+$ in near-surface aerosol associated with the major flow regimes that transport air to Bermuda do not mirror corresponding patterns in VWA $SO_4^{2-}$, $NO_3^-$, and $NH_4^+$ in precipitation (Fig. 2). Precipitation scavenges both soluble gases and particles from the column whereas the measured aerosol composition reflects near-surface conditions. In addition, relative to the column, near-surface air is chemically processed to a greater degree via transformations involving freshly produced, large, and short-lived marine aerosol; direct interactions with the ocean surface via the dry deposition of both precursor gases and particles; and, emissions of $(CH_3)_2S$ and, under clean conditions, $NH_3$ (e.g., Bouwman et al., 1997) from the ocean surface. These near-surface processes contribute to differential variability in the composition of near-surface aerosols and precipitation reported herein. These results imply that, relative to near-surface aerosols, the composition of precipitation may be a better indicator of column-integrated trends in soluble atmospheric constituents. We also note that aerosol sampling was sector controlled whereas precipitation sampling was not. However, available evidence suggests that local emissions have minor to negligible influences on the composition of wet-only precipitation at Bermuda (Galloway et al., 1988, 1989, 1993).

Trends in aerosol and precipitation composition associated with the NEUS/SEUS flow regime did not track corresponding trends in emissions over the US and Canada during the entire study period. Indeed, the significant and roughly similar proportionate decreases in VWA nss $SO_4^{2-}$ (factor of 2.2), $NO_3^-$ (factor of 1.9), and $NH_4^+$ (factor of 1.8) in precipitation associated with NEUS/SEUS flow between 1991 and 1996 (Figs. 2b, d, f) occurred in conjunction with reductions in $SO_2$ and $NO_x$ emissions over the US and Canada of only17% and 1%, respectively, and an increase on $NH_3$ emissions of 9% (Fig. 3). Corresponding patterns of decreasing particulate phase concentrations were not evident (Figs 2a, c, e). These results imply that physical processes such as trends in the efficiency of upwind removal via wet and dry deposition as opposed to trends in upwind emissions drove the similar variability evident in the VWA

concentrations of these species during this period. In this regard, we note that variability in mean precipitation amount per sample (Table 1) did not correlate with variability in VWA precipitation composition, which indicates that dilution effects associated with storm size (e.g., Galloway et al., 1989) was not a major factor driving interannual variability or trends in precipitation composition.

In contrast to the differences in concentrations associated with NEUS/SEUS flow and emissions in the US and Canada evident in our data, between 1980 and 2010, wet-deposition fluxes of $SO_4^{2-}$ via precipitation and particulate $SO_4^{2-}$ concentrations in near-surface air over the eastern US decreased by 58% and 40%, respectively and the corresponding $SO_2$ emissions over the US decreased by 56% (Leibensperger et al. 2012). Between 1980 and 2009, wet deposition fluxes of $NO_3^-$ over the eastern US decreased 33% while corresponding $NO_x$ emissions decreased 36%. Particulate $NO_3^-$ concentrations over the eastern US were relatively uniform from 1990 to 2000 but decreased by 23% between 2000 and 2009 (Leibensperger et al. 2012). Wet deposition fluxes of $NH_4^+$ over the eastern US during this period exhibited no significant trend whereas the corresponding particulate $NH_4^+$ concentrations decrease by 30%. Comparisons with measurements suggest that model calculations of these trends significantly underestimate the decreases in particulate $NO_3^-$ and $NH_4^+$ over this period (Leibensperger et al., 2012). Measured and simulated trends over the downwind western NAO were not reported.

It is evident from the above that temporal variability in (1) spatial distributions of emission fields over the NEUS/SEUS source region during the period of record, (2) the spatial distribution of transport within the NEUS/SEUS flow regime, and/or (3) spatial distributions of deposition fields under NEUS/SEUS flow contributed to temporal variability in aerosol and precipitation composition at Bermuda. However, available information, and particularly the lack of spatially resolved measurements of aerosol and precipitation composition over the western NAO precludes quantitative evaluation of these factors. Our results highlight the difficulty in characterizing influences of emissions reductions based on measurements at individual sites located downwind.

Despite these limitations, results do provide unique insight regarding long-term trends in regional atmospheric composition. For example, although only the trend in particulate $NO_3^-$ was marginally significant, all trends in $NO_3^-$ and $NH_4^+$ associated with aerosols and precipitation sampled under Oceanic flow over the period of record were positive and within a factor of about 2 in magnitude (31% to 67%. Fig. 2c,d,e, and f). The consistency of these patterns suggests that background concentrations of inorganic N species in aged marine air within the NAO basin may have increased over the past two decades. In contrast, the corresponding concentrations of VWA nss $SO_4^{2-}$ in precipitation associated with Oceanic flow decreased significantly (Fig. 2b, Table 2).

The changing mixture of acids and bases in the NAO troposphere impacts pH-dependent chemical processes including the phase partitioning and associated atmospheric lifetimes against deposition for compounds with pH-dependent solubilities. For example, trends of both aerosols and precipitation based on all data (Fig. 1, Table 2) and the subset of data associated with NEUS/SEUS flow (Fig. 2, Table 2) suggest that, on average, concentrations of nss $SO_4^{2-}$ decreased, $NH_4^+$ remained essentially unchanged or increased, and $NO_3^-$ remained essentially unchanged over the period of record. As discussed in Section 2.3, negative bias in particulate

$NH_4^+$ resulting from artifact volatilization of $NH_3$ from aerosol sampled in bulk during the early part of the record may have contributed to the positive trend in particulate $NH_4^+$ but the positive trend for precipitation is not subject to such artifacts. These data imply that, on average, acidities of sub-μm-diameter aerosol solutions, with which most particulate nss $SO_4^{2-}$ and $NH_4^+$ at Bermuda was associated (Moody et al., 2014), decreased over the period, particularly during the earlier part of the record. Decreasing aerosol acidities would have shifted the phase partitioning of total $NH_3$ ($NH_3 + NH_4^+$) towards the gas phase (e.g., Smith et al., 2007) as is evident in the changing molar ratios of nss $SO_4^{2-}$ to $NH_4^+$ over the period (Fig. 5). For example, based on the trend lines (Fig. 2, Table 2), between 1989 and 2009, ratios of mean nss $SO_4^{2-}$ to $NH_4^+$ in near-surface aerosols associated with NEUS/SEUS flow decreased from 1.2 to 1.1 (factor of 1.1) whereas the corresponding ratios for VWA concentrations in precipitation decreased from 2.0 to 0.48 (factor of 4.3). The greater decrease in ratios for precipitation suggests that relative contributions to $NH_4^+$ in precipitation from the scavenging of gaseous $NH_3$ versus particulate $NH_4^+$ increased over the period. This increase in relative contributions from $NH_3$ would be consistent with expectations based on a pH-dependent shift in the phase partitioning of total $NH_3$ towards the gas phase coupled with efficient scavenging of both $NH_3$ and particulate $NH_4^+$ by precipitation. In addition, because dry deposition velocities to the ocean surface for $NH_3$ are greater than those for sub-μm aerosol size fractions with which most $NH_4^+$ is associated in ambient air (Smith et al., 2007; Moody et al., 2014), this shift would have resulted in an increase in the average dry-deposition flux of total $NH_3$ to the ocean surface, a corresponding decrease in the fraction of total $NH_3$ removed via wet deposition, and a decrease in the atmospheric lifetime of total $NH_3$ against wet plus dry deposition. The long-term change in atmospheric acidity is also evident in the significant decrease (37%) in VWA $H^+$ associated with precipitation sampled under NEUS/SEUS flow over the period of record (SLR slope = -0.29, $r^2 = 0.49$, Fig. 6). We recognize that trends reported herein are associated with large uncertainties, the corresponding changes in phase partition and deposition are nonlinear, and explicit evaluation of trends in aerosol solution pH and associated implications are not possible without paired measurements of particulate and gas phase species. However, these relationships provide relevant quantitative context for aspects of S and N cycling over the North Atlantic that are driven by changing emissions over surrounding continents.

Despite the larger interannual variability evident in the temporal trends, our measurements and associated interpretations suggest that concentrations and deposition fluxes of total $NH_3$ over the western NAO increased during the period of record. However, EPA (2013) and Environment Canada (2014) indicate that $NH_3$ emissions in the US and Canada did not vary significantly between 1990 and 2009. If regionally representative, our results suggest the possibility that these inventories may underestimate increasing trends in $NH_3$ emissions over North America. Alternatively, increasing transport of $NH_3$ and particulate $NH_4^+$ from more distant sources in Asia may have contributed to rising atmospheric concentrations over the NAO. In this regard, Moody et al. (2014) detected significant mineral aerosol associated with NEUS flow that available evidence suggests originated in Asia. Other studies have reported that the transport of emission products from Asia significantly impact air quality over the western US although corresponding impacts in the eastern US are relatively small to negligible (e.g., Koch et al., 2007; Lin et al., 2014).

Because $HNO_3$ partitions primarily with less-acidic super-μm-diameter aerosols, its cycling in marine air is largely decoupled from that of $NH_3$. In addition, most acidity added to larger aerosol size fractions via accumulation of $HNO_3$ and $H_2SO_4$ is displaced to the gas phase in association with HCl volatilization, which acts to regulate the pH of super-μm marine aerosols to a fairly narrow range (low 3s to high 4s) over highly variable chemical regimes (e.g., Keene et al., 2009). Consequently, relative to $NH_3$, $HNO_3$ cycling over the ocean is less sensitive to changes in atmospheric acidity. Similarly, particulate $NO_3^-$ is also less sensitive than $NH_4^+$ to artifact volatilization from marine aerosol sampled in bulk.

Our results also provide insight regarding the potential influence of reductions in $SO_2$ emissions from North America on direct radiative forcing by pollutant aerosols over the western NAO at Bermuda. Assuming that the marginally insignificant trend in particulate nss $SO_4^{2-}$ associated with NEUS/SEUS flow is reasonably representative of the actual long-term decline, the SLR indicates that between 1989 and 2009, annual average concentrations for this flow regime decreased by roughly 2.4 nmol $m^{-3}$ or about 10% (Fig. 2a, Table 2). A regression fit to the scatter plot of satellite AOD at 550 nm versus nss $SO_4^{2-}$ associated with near-surface aerosol under NEUS flow regime during 2006 to 2009 reported by Moody et al. (2014) yields a slope of 0.002 $nmol^{-1}$ $m^3$. Assuming that trends in other aerosol constituents that scatter and/or absorb radiation under this flow regime co-varied with particulate nss $SO_4^{2-}$, the corresponding decrease in AOD (0.005) coupled with satellite-derived estimates for the radiative efficiency of aerosols per unit AOD in North American outflow over the ocean (-27 to -60 W $m^{-2}$ $\delta^{-1}$) (Anderson et al., 2005) yield an estimated net warming of 0.1 to 0.3 W $m^{-2}$ that resulted from the decreased shortwave scattering and absorption by nss $SO_4^{2-}$ and associated aerosol constituents under NEUS/SEUS flow at Bermuda between 1989 and 2009. As discussed above, the greater decreasing trend for nss $SO_4^{2-}$ in precipitation relative to near-surface aerosols suggests that the decline in particulate nss $SO_4^{2-}$ in near surface air was less than that for oxidized S in the column scavenged by precipitation. Consequently, this estimated range in warming should be considered a lower limit. We appreciate that this approach is associated with large and poorly constrained uncertainties but it is reasonably consistent with expectations based on model estimates of the trend in net radiative warming of 0.8 W $m^{-2}$ over the US resulting from the reduction in scattering and absorption by pollutant aerosols between 1990 and 2010 (Leibensperger et al., 2012).

## 4.0. Summary

Since the 1980s, mandated reductions in $SO_2$ and $NO_x$ emissions in the US, Canada, and Europe have resulted in decreased export of oxidized S and N compounds to the NAO atmosphere. Measurements at Bermuda between 1989 and 2009 indicate that nss $SO_4^{2-}$ associated with aerosols and precipitation decreased significantly (22% and 49%, respectively) whereas $NH_4^+$ associated with precipitation increased significantly (70%) (Fig. 1, Table 2). Corresponding trends in $NO_3^-$ associated with aerosols and precipitation and of particulate $NH_4^+$ were insignificant.

To assess influences of emissions in upwind regions, data were stratified based on FLEXPART retroplumes into four discrete transport regimes. Nss $SO_4^{2-}$ in precipitation during NEUS/SEUS and Oceanic flow decreased significantly (61% each) whereas corresponding trends in nss $SO_4^{2-}$

748 associated with near-surface aerosols for both flow regimes were insignificant (Fig. 2a,b, Table
749 2). Available evidence supports the hypothesis that, for these flow regimes, ratios of
750 anthropogenic to biogenic contributions to nss $SO_4^{2-}$ in the column scavenged by precipitation
751 were relatively greater than those for near-surface aerosol and, thus, precipitation provided a
752 better indicator of column-integrated trends.
753
754 Particulate nss $SO_4^{2-}$ under African flow also decreased significantly (34%) whereas the
755 corresponding decrease in nss $SO_4^{2-}$ associated with precipitation was insignificant (Fig. 2a,b,
756 Table 2). We infer that these trends were driven in part by reductions in the emissions and
757 transport of oxidized S compounds from Europe.
758
759 Insignificant trends in $NO_3^-$ associated with aerosols and precipitation under NEUS/SEUS flow
760 (Fig. 2c,d, Table 2) did not reflect the large decrease in $NO_x$ emissions in the US and Canada
761 over the period of record (Fig. 3). The rapid oxidation of $NO_x$ in marine air coupled with
762 partitioning of most $HNO_3$ with large, short-lived marine aerosol may have attenuated trends in
763 $NO_3^-$ concentrations relative to upwind $NO_x$ emissions.
764
765 Trends of both aerosols and precipitation based on all data (Fig. 1) and the subset of data
766 associated with NEUS/SEUS flow (Fig. 2) suggest that, on average, concentrations of nss $SO_4^{2-}$
767 decreased, $NH_4^+$ remained essentially unchanged or increased, and $NO_3^-$ remained essentially
768 unchanged, which implies that the total amount of acidity in the multiphase gas-aerosol system
769 in the western NAO troposphere decreased over the period of record. This interpretation is
770 consistent with the decreasing trend in VWA $H^+$ in precipitation under NEUS/SEUS flow
771 (Figure 6). The inferred decrease in aerosol acidities would have (1) shifted the phase
772 partitioning of total $NH_3$ towards the gas phase, (2) increased the dry deposition velocities for
773 total $NH_3$ to the ocean surface, (3) increased relative contributions to $NH_4^+$ in precipitation from
774 the scavenging of gaseous $NH_3$ versus particulate $NH_4^+$, and (4) decreased the atmospheric
775 lifetime of total $NH_3$ against wet plus dry deposition.
776
777 Assuming that the marginally insignificant trend in particulate nss $SO_4^{2-}$ in near-surface air
778 associated with NEUS/SEUS flow is reasonably representative of long-term temporal variability
779 (Fig. 2a, Table 2), decreasing concentrations over the period of record suggest a lower limit for
780 net warming in the range of 0.1 to 0.3 W $m^{-2}$ resulting from decreased shortwave scattering and
781 absorption by nss $SO_4^{2-}$ and associated aerosol constituents transported from North America over
782 the western NAO.
783
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Table 1. Numbers (Ns) of daily aerosol and precipitation samples and mean precipitation amounts (cm) per sample for all data evaluated in this study partitioned by flow regime and year. Annual data for 1989 through 1997 are binned by calendar year (1 January through 31 December) and those for 2006 through 2009 are binned from 1 July through 30 June.

| ***Mid Year*** | 1989 | 1990 | 1991 | 1992 | 1993 | 1994 | 1995 | 1996 | 1997 | 2007 | 2008 | 2009 | All |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| ***Aerosols, N*** | | | | | | | | | | | | | |
| All Data[1] | 168 | 184 | 199 | 186 | 130 | 152 | 174 | 182 | 215 | 113 | 111 | 84 | 1898 |
| NEUS/SEUS | 119 | N/A | 136 | 107 | 95 | 101 | 104 | 132 | 133 | 64 | 68 | 54 | 1113 |
| Africa | 30 | N/A | 41 | 45 | 24 | 28 | 40 | 32 | 49 | 26 | 30 | 22 | 367 |
| Oceanic | 9 | N/A | 11 | 17 | 3 | 11 | 9 | 8 | 10 | 6 | 8 | 5 | 97 |
| North | 10 | N/A | 11 | 17 | 8 | 12 | 21 | 10 | 23 | 17 | 5 | 3 | 137 |
| ***Precipitation, N*** | | | | | | | | | | | | | |
| All Data[2] | 101 | 72 | 71 | 70 | 76 | 82 | 76 | 84 | N/A | 99 | 100 | 86 | 917 |
| NEUS/SEUS | 59 | N/A | 43 | 37 | 51 | 46 | 42 | 53 | N/A | 61 | 55 | 40 | 487 |
| Africa | 34 | N/A | 15 | 17 | 17 | 19 | 17 | 20 | N/A | 19 | 21 | 34 | 213 |
| Oceanic | 5 | N/A | 5 | 9 | 3 | 7 | 7 | 6 | N/A | 10 | 11 | 6 | 69 |
| North | 3 | N/A | 8 | 7 | 5 | 10 | 10 | 5 | N/A | 9 | 13 | 6 | 76 |
| ***Precipitation amount, cm*** | | | | | | | | | | | | | |
| All Data | 0.87 | 1.08 | 1.09 | 1.15 | 1.66 | 1.39 | 1.06 | 1.08 | N/A | 0.94 | 1.02 | 0.83 | 1.09 |
| NEUS/SEUS | 0.81 | N/A | 0.89 | 1.08 | 1.71 | 1.36 | 1.21 | 1.06 | N/A | 0.95 | 1.05 | 0.79 | 1.09 |
| Africa | 1.02 | N/A | 1.07 | 1.35 | 1.36 | 1.32 | 0.97 | 1.43 | N/A | 1.07 | 1.02 | 0.77 | 1.10 |
| Oceanic | 0.90 | N/A | 0.56 | 1.28 | 1.00 | 1.93 | 1.06 | 0.51 | N/A | 1.11 | 0.76 | 0.99 | 1.03 |
| North | 0.35 | N/A | 2.53 | 0.90 | 2.49 | 1.31 | 0.60 | 0.57 | N/A | 0.36 | 1.14 | 1.31 | 1.16 |

N/A indicates that either the chemical data or the corresponding FLEXPART retroplumes were not available for the indicated period (see text).

[1]Ns correspond to particulate nss $SO_4^{2-}$, $NO_3^-$, and $NH_4^+$; for particulate $CH_3SO_3^-$, total N was 1266 due to the shorter period of record and relatively fewer samples with concentrations greater than DLs.

[2]Ns corresponds to nss $SO_4^{2-}$, $NO_3^-$, and $NH_4^+$ in precipitation; for $CH_3SO_3^-$ in precipitation, total N was 845 due to the relatively fewer samples with concentrations greater than DLs.

Table 2. Regression statistics and, for significant trends, percent changes in concentrations over the period of record.

| Species / Flow Regime | Bootstrap Slope (Std.Error) (nmol $m^{-3}$ $yr^{-1}$) | SLR Slope(nmol $m^{-3}$ $yr^{-1}$) | SLR $r^2$ | SLR Change[1] (%) | Bootstrap Slope (Std. Error) (μmol $L^{-1}$ $yr^{-1}$) | SLR Slope (μmol $L^{-1}$ $yr^{-1}$) | SLR $r^2$ | SLR Change[1] (%) |
|---|---|---|---|---|---|---|---|---|
| | **Aerosol** | | | | **Precipitation** | | | |
| ***nss $SO_4^{2-}$*** | | | | | | | | |
| All Data | -0.26(0.08)* | -0.24 | 0.17 | -22% | -0.10(0.03)* | -0.11 | 0.67 | -49% |
| NEUS/SEUS | -0.16(0.11) | -0.12 | - | - | -0.16(0.05)* | -0.17 | 0.61 | -61% |
| Africa | -0.28(0.12)* | -0.31 | 0.29 | -34% | -0.06(0.06) | -0.06 | - | - |
| Oceanic | 0.14(0.12) | 0.14 | - | - | -0.09(0.03)* | -0.08 | 0.31 | -61% |
| North | 0.36(0.34) | 0.22 | - | - | 0.10(0.06) | 0.04 | - | - |
| ***$NO_3^-$*** | | | | | | | | |
| All Data | -0.01(0.05) | -0.01 | - | - | 0.05(0.03) | 0.04 | - | - |
| NEUS/SEUS | 0.03(0.07) | 0.03 | - | - | 0.02(0.05) | 0.01 | - | - |
| Africa | -0.12(0.06)** | -0.13 | 0.26 | -20% | 0.08(0.05) | 0.07 | - | - |
| Oceanic | 0.17(. 09)** | 0.18 | 0.53 | 46% | 0.06(0.05) | 0.06 | - | - |
| North | 0.23(0.17) | 0.31 | - | - | 0.17(0.06)* | 0.13 | 0.32 | 76% |
| ***$NH_4^+$*** | | | | | | | | |
| All Data | -0.05(0.08) | -0.06 | - | - | 0.08(0.03)* | 0.08 | 0.68 | 70% |
| NEUS/SEUS | 0.05(0.10) | 0.04 | - | - | 0.08(0.05) | 0.09 | - | - |
| Africa | -0.33(0.11)* | -0.33 | 0.35 | -44% | 0.09(0.05)** | 0.09 | 0.48 | 102% |
| Oceanic | 0.05(0.16) | 0.09 | - | - | 0.03(0.03) | 0.03 | - | - |
| North | 0.15(0.26) | 0.05 | - | - | 0.09(0.06) | 0.05 | - | - |

* $p = 0.05$; significant at 95% confidence.

** $p = 0.10$; significant at 90% confidence.

[1]Percent change over the period of record relative to 1989 based on the SLR slope.

Figure Caption

Figure 1. Temporal trends in (a) annual average concentrations of bulk particulate nss $SO_4^{2-}$ (red), $NO_3^-$ (blue), and $NH_4^+$ (green) in near-surface air (white backgrounds) and (b) corresponding annual VWA concentrations in precipitation (light blue backgrounds) at Bermuda based on all quality-assured data generated over the period of record. Color-coded dashed lines correspond to SLRs for annual averages and VWAs versus time.

Figure 2. Temporal trends in annual average concentrations of bulk particulate (a) nss $SO_4^{2-}$, (c) $NO_3^-$, and (e) $NH_4^+$ in near-surface air (white backgrounds) and annual VWA concentrations of (b) nss $SO_4^{2-}$, (d) $NO_3^-$, and (f) $NH_4^+$ in precipitation (light bluet backgrounds) associated with NEUS/SEUS (red), African (yellow), Oceanic (blue), and North (green) flow regimes. Color-coded dashed lines correspond to SLRs for annual mean and VWA concentrations versus time.

Figure 3. Temporal trends in $SO_2$ (red), $NO_x$ (blue), and $NH_3$ (green) emitted to the atmosphere over the continental US (EPA, 2013) and over the continental US plus Canada (Environment Canada, 2014; solid line) during the period of this study.

Figure 4. Temporal trends in anthropogenic and biogenic contributions to nss $SO_4^{2-}$ associated with (a) aerosols (white backgrounds) and (b) precipitation (light blue backgrounds) sampled under NEUS/SEUS flow.

Figure 5. Temporal trends in (a) ratios of annual mean concentrations of particulate nss $SO_4^{2-}$ versus $NH_4^+$ (white backgrounds) and (b) corresponding ratios of annual VWA concentrations in precipitation (light blue backgrounds) associated with NEUS/SEUS (red), African (yellow), Oceanic (blue), and North (green) flow regimes and for all data (black).

Figure 6. Temporal trend in annual VWA $H^+$ in precipitation associated with NEUS/SEUS flow.

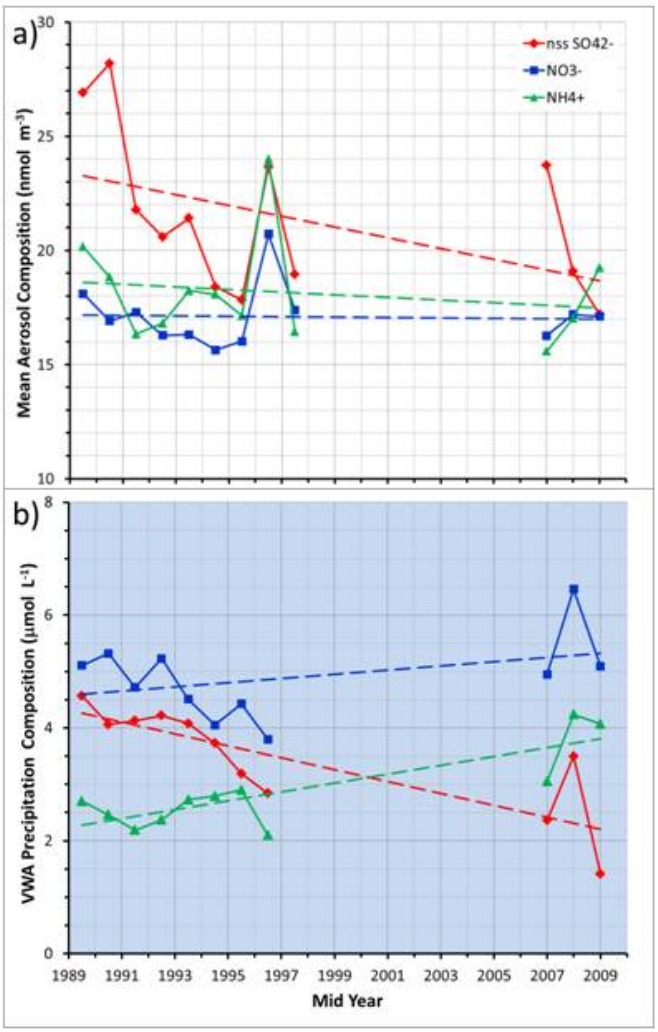
a)
b)
nss SO42-
NO3-
NH4+
Mean Aerosol Composition (nmol m⁻³)
VWA Precipitation Composition (µmol L⁻¹)
Mid Year
30
25
20
15
10
8
6
4
2
0
1989
1991
1993
1995
1997
1999
2001
2003
2005
2007
2009

Figure 1

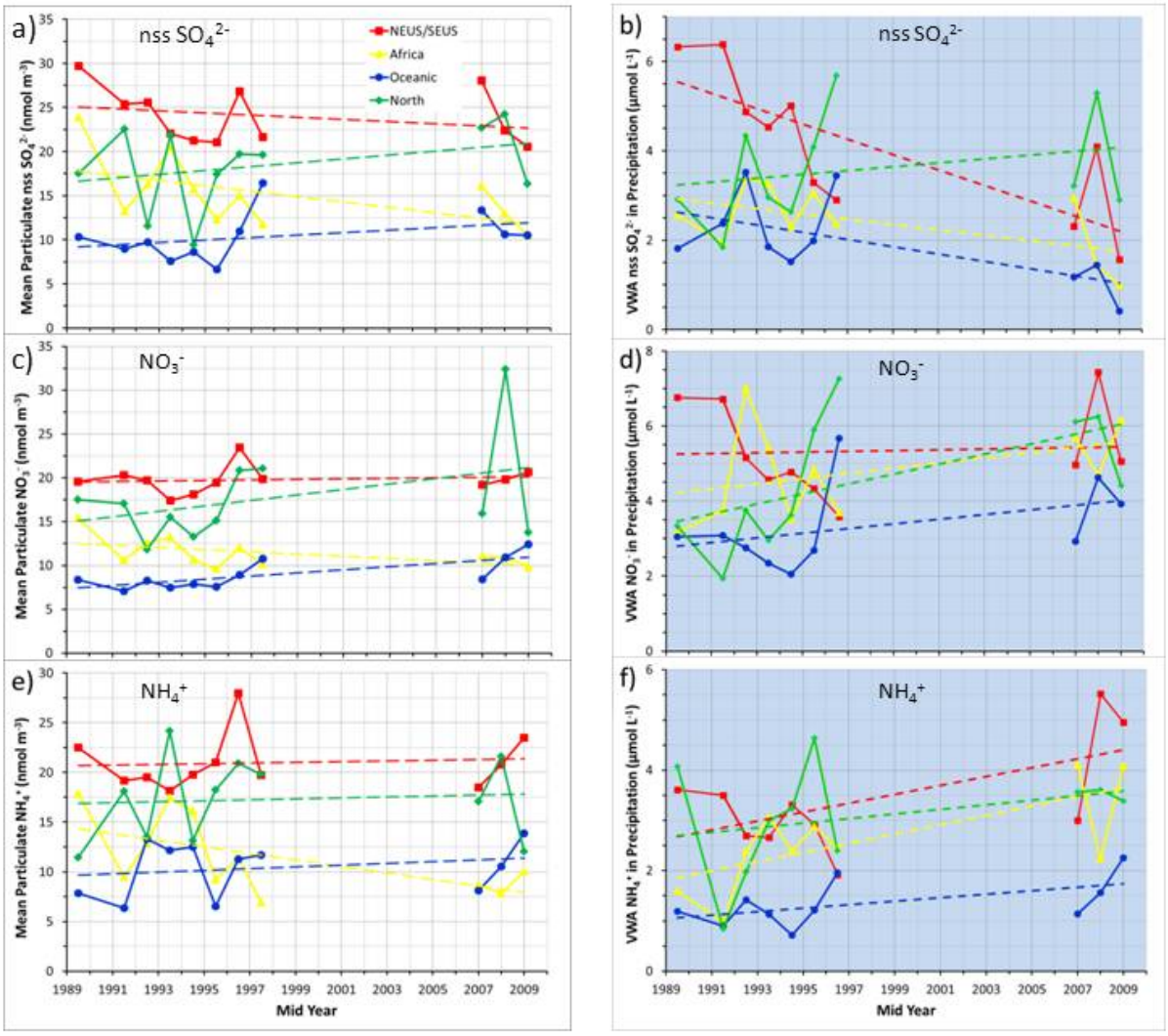
a)
nss $SO_4^{2-}$
NEUS/SEUS
Africa
Oceanic
North
Mean Particulate nss $SO_4^{2-}$ (nmol $m^{-3}$)
b)
nss $SO_4^{2-}$
VWA nss $SO_4^{2-}$ in Precipitation (µmol $L^{-1}$)
c)
$NO_3^-$
Mean Particulate $NO_3^-$ (nmol $m^{-3}$)
d)
$NO_3^-$
VWA $NO_3^-$ in Precipitation (µmol $L^{-1}$)
e)
$NH_4^+$
Mean Particulate $NH_4^+$ (nmol $m^{-3}$)
f)
$NH_4^+$
VWA $NH_4^+$ in Precipitation (µmol $L^{-1}$)
1989 1991 1993 1995 1997 1999 2001 2003 2005 2007 2009
Mid Year

Figure 2

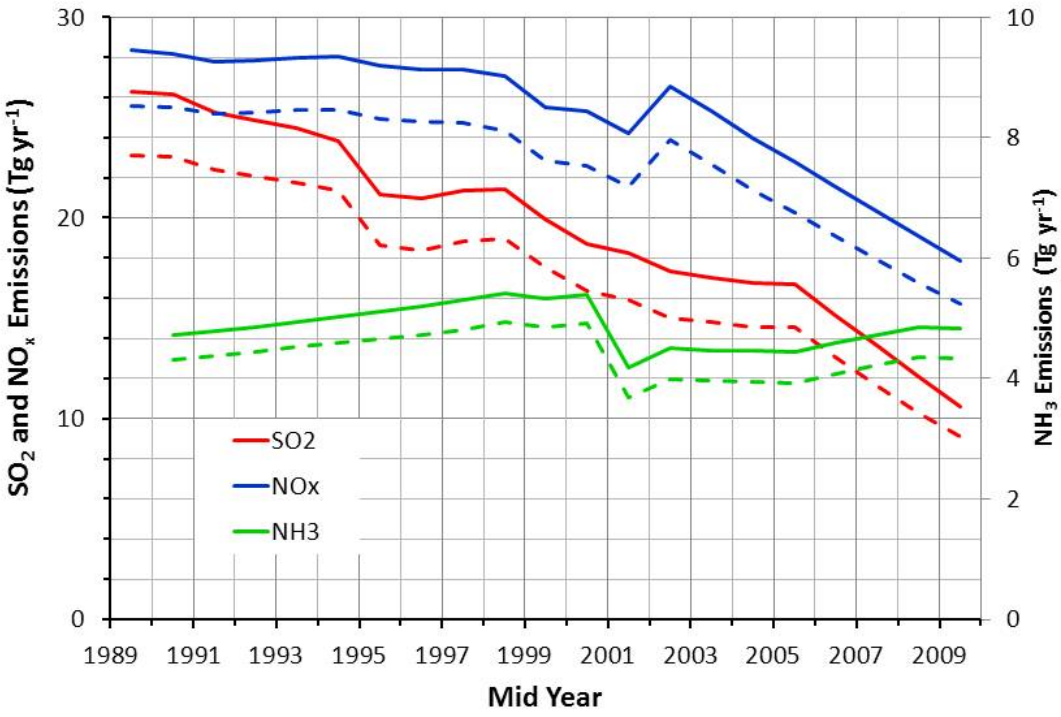
30
20
10
0
10
8
6
4
2
0
1989
1991
1993
1995
1997
1999
2001
2003
2005
2007
2009
Mid Year
SO2
NOx
NH3
SO2 and NOx Emissions (Tg yr-1)
NH3 Emissions (Tg yr-1)

Figure 3

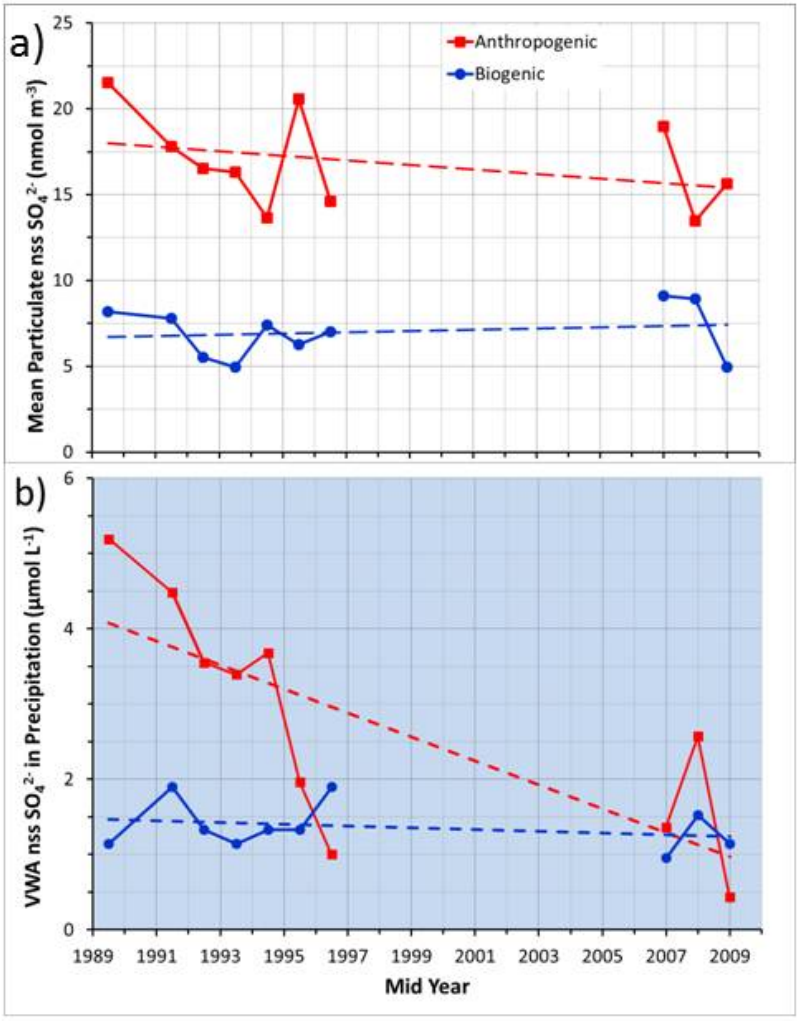
a)
Anthropogenic
Biogenic
Mean Particulate nss $SO_4^{2-}$ (nmol $m^{-3}$)
25
20
15
10
5
0
b)
VWA nss $SO_4^{2-}$ in Precipitation (µmol $L^{-1}$)
6
4
2
0
1989
1991
1993
1995
1997
1999
2001
2003
2005
2007
2009
Mid Year

Figure 4

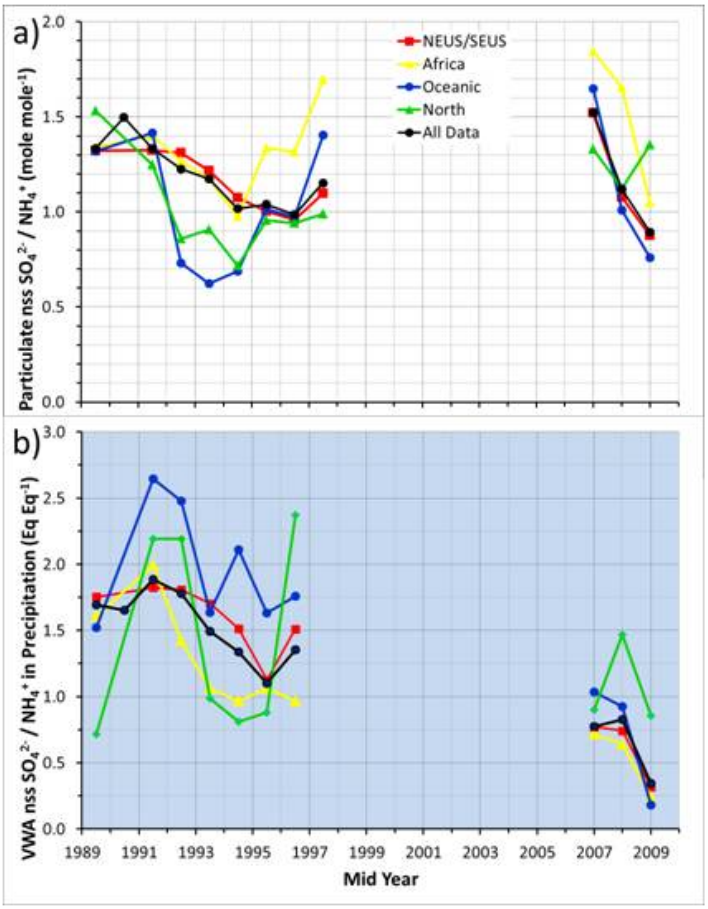
a)
b)
NEUS/SEUS
Africa
Oceanic
North
All Data
Particulate nss $SO_4^{2-}$ / $NH_4^+$ (mole mole$^{-1}$)
VWA nss $SO_4^{2-}$ / $NH_4^+$ in Precipitation (Eq Eq$^{-1}$)
Mid Year
0.0
0.5
1.0
1.5
2.0
2.5
3.0
1989
1991
1993
1995
1997
1999
2001
2003
2005
2007
2009

Figure 5

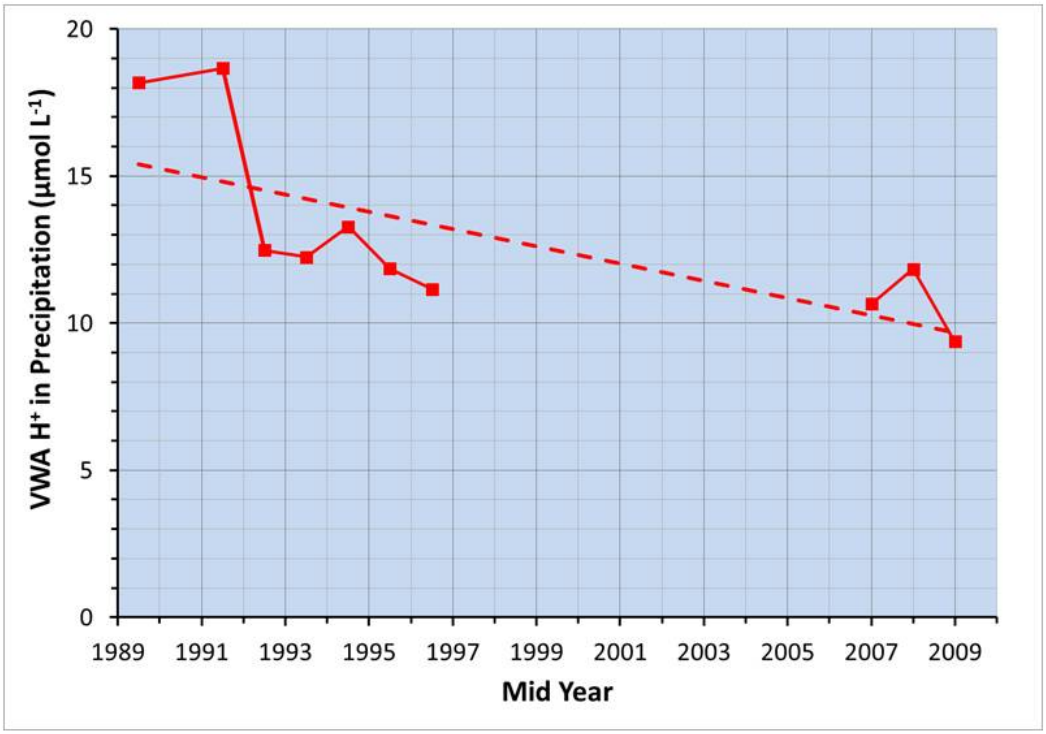
20
15
10
5
0
VWA H+ in Precipitation (µmol L-1)
1989
1991
1993
1995
1997
1999
2001
2003
2005
2007
2009
Mid Year

Figure 6