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Air quality and atmospheric deposition in the eastern US: 20 years of change

J. E. Sickles II[1] **and D. S. Shadwick**[2,†]

[1]Landscape Characterization Branch, Environmental Sciences Division, National Exposure Research Laboratory, United States Environmental Protection Agency, Research Triangle Park, North Carolina 27711, USA
[2]Computer Sciences Corporation, Durham, North Carolina 27713, USA
[†]deceased

Correspondence to: J. E. Sickles II (sickles.joseph@epa.gov)

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Abstract. Data collected in the eastern US between 1990 and 2009 at 34 paired dry and wet monitoring sites are examined. A goal is to evaluate the air quality impacts occurring between 1990 and 2009 that are associated with concurrent legislatively mandated changes in emissions. Four 5-year periods, 1990–1994 (P1), 1995–1999 (P2), 2000–2004 (P3), and 2005–2009 (P4) are considered, with a primary focus on P1-to-P4 changes. Results suggest that legislatively mandated air pollution mitigation strategies have been successful in improving air quality and reducing atmospheric deposition in the eastern US.

Respective P1-to-P4 reductions of estimated sulfur dioxide (SO_2) and nitrogen oxides (NO_x) emissions in the eastern US are 50 and 42 %. Corresponding behavior of the following metrics associated with these emissions reductions is examined: monitored atmospheric concentrations of SO_2, aerosol sulfate (SO_4), and oxidized sulfur (S); dry, wet, and total deposition of S; monitored atmospheric concentrations of nitric acid (HNO_3), aerosol nitrate (NO_3), and their sum, oxidized nitrogen (OxN); dry, wet, and total deposition of OxN; monitored atmospheric concentration of aerosol ammonium (NH_4); dry, wet, and total deposition of NH_4; summed monitored atmospheric concentration of oxidized and reduced nitrogen (N); dry, wet, and total deposition of N; wet deposition of hydrogen ion (H^+); monitored atmospheric concentration of ozone (O_3); dry deposition of O_3; and the summed monitored atmospheric concentration of aerosol NO_3, SO_4, and NH_4 (Clean Air Status and Trends Network particulate matter – CASTNET PM). Other metrics (e.g., ratios of dry to total deposition) are also considered.

Selected period-to-period changes of air quality and deposition metrics at site, regional, and seasonal scales are discussed. As an example, despite P1-to-P3 reductions in estimated emissions of both SO_2 and NO_x, aerosol NO_3 concentration increased in the east, with widespread wintertime numerical increases in both aerosol NO_3 concentration and CASTNET PM. However, a reversal of this behavior is associated with continuing P3-to-P4 reductions of SO_2 and NO_x emissions. Thus, additional P3-to-P4 reductions of these emissions, especially NO_x, appear to have made progress in altering the chemical regime of the wintertime eastern US atmosphere so that future emissions reductions and their resulting reductions in aerosol concentrations may no longer be accompanied by sub-linear changes (or actual increases) in CASTNET PM.

1 Introduction

In the United States (US), pollution control legislation has been established to protect the public health and welfare by reducing emissions of selected pollutants. Both sulfur dioxide (SO_2) and nitrogen dioxide (NO_2) are designated by the US Environmental Protection Agency (EPA) as criteria pollutants, and they contribute to acidic deposition as well as airborne particulate matter (PM). In addition, nitrogen ox-

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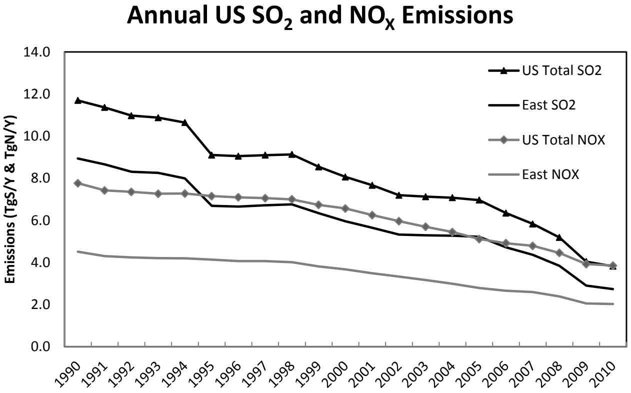


Figure 1. Annual US SO_2 (Tg S) and NO_x (Tg N) emissions estimates between 1990 and 2010 (Xing et al., 2013).

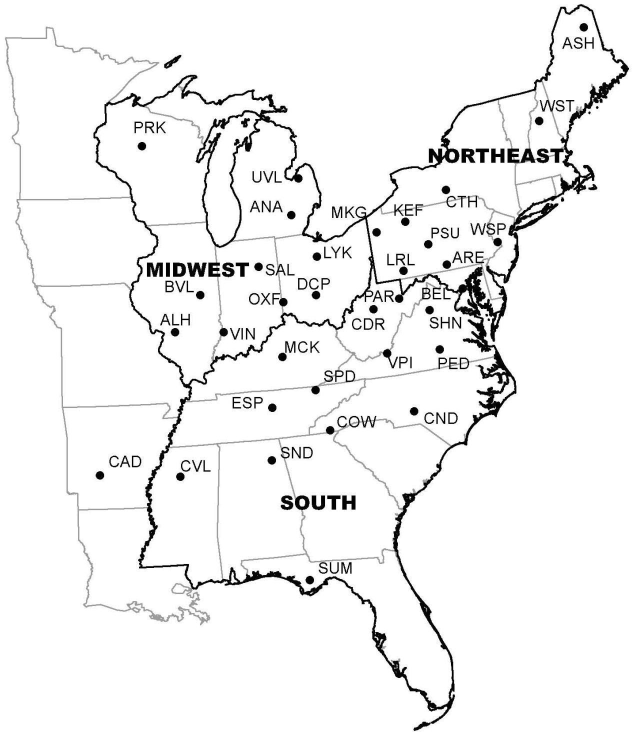


Figure 2. CASTNET monitoring sites and geographical regions considered in the current study (see Table 1).

ides (NO_x), the sum of nitric oxide (NO) and NO_2, act as precursors of another criteria pollutant, ozone (O_3).

Nationwide, in 1990, 69 % of SO_2 emissions came from electric generating units (EGUs), whereas 82 % of NO_x emissions came from the sum of EGUs (25 %) and mobile sources (57 %) (Xing et al., 2013). Sources in the eastern states contributed 76 and 58 % of the US total 1990 SO_2 and NO_x emissions, respectively. The Clean Air Act Amendments of 1990 (CAAA) established phased year-round controls for SO_2 and NO_x emissions from EGUs that became effective in 1995 for SO_2 and 1996 for NO_x (Phase I), while additional controls became effective under Phase II in 2000. Over half of the EGUs targeted by the CAAA are located in six states along the Ohio River (source region – SR; Table 1). Beginning in 1999, O_3 season (i.e., summertime) NO_x controls focusing on EGUs became effective in selected eastern states under the Ozone Transport Commission (OTC) and were superceded in 2003 by the NO_x State Implementation Plan (SIP) Call. The affected states chose to meet their mandatory reductions by participating in the NO_x Budget Trading Program (BTP), a market-based cap and trade program for EGUs and large industrial units. The BTP was replaced in 2009 by the Clean Air Interstate Rule (CAIR). Various mobile source NO_x emissions control programs also began in the mid- to late 1990s. Fully implemented in 2006, the Tier 2 Gasoline Sulfur Program targeted both SO_2 and NO_x emissions from mobile sources. These mobile source programs have a cumulative effect of reducing emissions over time as the mobile fleet is replaced.

Figure 1 shows estimates of emissions from 1990 to 2010 for both the total US and the eastern states (Xing et al., 2013). Both SO_2 and NO_x emissions show weak reductions between 1990 and 1994. There is a sharp reduction in SO_2 emissions in 1995, when Phase I controls became effective. Although additional reductions of both SO_2 and NO_x emissions begin to appear in 1999, they are apparent in later years (e.g., after 2005 for SO_2). Although a substantial portion of the long-term emissions reductions since 1990 has resulted from legislatively driven emissions controls, economic factors (e.g., coal-to-natural gas fuel switching and recession-induced reduction in demand for electricity and transportation fuel) played a sizeable role between 2008 and 2009 (Lu et al., 2012).

A major objective of the current study is to examine the monitored and estimated air quality and deposition behaviors in the eastern US (E) between 1990 and 2009 associated with changes in emissions. The time period of interest is divided into four 5-year periods: 1990–1994 (period one, P1), 1995–1999 (period two, P2), 2000–2004 (period three, P3), and 2005–2009 (period four, P4). Focusing on these 5-year periods, average P1 US SO_2 and NO_x emissions have declined by 19 and 6 % by P2, by 33 and 19 % by P3, and by 49 and 37 % by P4 (Xing et al., 2013). In the current study, the east is taken to represent all states east of the Mississippi River and is divided into three geographical regions: midwest (MW), northeast (NE), and south (SO) (Fig. 2). Mean period-specific emissions in these regions are illustrated for each 5-year period relative to P1 in Fig. 3.

This paper builds on the previous work (Sickles and Shadwick, 2007a and b; hereafter known as SS07a and SS07b). In SS07a seasonal and regional distributions of concentration and deposition of selected pollutants were examined for the 1990s (i.e., P1 and P2) at eastern rural US Clean Air Status and Trends Network (CASTNET) and paired National Atmospheric Deposition Program (NADP) monitoring sites.

Table 1. Summary of characteristics of 34 CASTNET monitoring sites providing data in current study (see Fig. 2) listed by region.

Site	Name	Land use[a]	Terrain[b]	Elevation (m)	Region[d]	Special category[e]	Latitude (° N)	Longitude (° W)
ALH	Alhambra, IL	A	FL	164	MW	SR	38.9	89.6
ANA	Ann Arbor, MI	F	FL	267	MW		42.6	83.9
BVL	Bondville, IL	A	FL	212	MW	SR	40.1	88.4
DCP	Deer Creek State Park, OH	A	R	265	MW	SR	39.6	83.3
LYK	Lykens, OH	A	FL	303	MW	SR	40.9	83.0
OXF	Oxford, OH	A	R[c]	284	MW	SR	39.5	84.7
PRK	Perkinstown, WI	A	R	472	MW	BKG	45.2	90.6
SAL	Salamonie Reservoir, IN	A	FL	249	MW	SR	40.8	85.7
UVL	Unionville, MI	A	FL	210	MW		43.6	83.4
VIN	Vincennes, IN	A	R	134	MW	SR	38.7	87.5
ARE	Arendtsville, PA	A	R	269	NE	SR	39.9	77.3
ASH	Ashland, ME	A	FL	235	NE	BKG	46.6	68.4
BEL	Beltsville, MD	S/A	FL	46	NE		39.0	76.8
CTH	Connecticut Hill, NY	F	R[c]	515	NE	HE	42.4	76.7
KEF	Kane Experimental Forest, PA	F	R	622	NE	SR	41.6	78.8
LRL	Laurel Hill State Park, PA	F	C[c]	615	NE	SR	40.0	79.2
MKG	M.K. Goddard State Park, PA	F	R[c]	384	NE	SR	41.4	80.2
PSU	Penn. State University, PA	A	R	378	NE	SR	40.7	77.9
WSP	Washington's Crossing, NJ	A/S	R	58	NE		40.3	74.9
WST	Woodstock, NH	F	C[c]	258	NE		43.9	71.7
CAD	Caddo Valley, AR	F	R[c]	71	SO	BKG	34.2	93.1
CDR	Cedar Creek State Park, WV	F	C[c]	234	SO	SR	38.9	80.9
CND	Candor, NC	F	R	198	SO		35.3	79.8
COW	Coweeta, NC	F	C[c]	686	SO		35.1	83.4
CVL	Coffeeville, MS	F	R	134	SO		34.0	89.8
ESP	Edgar Evins State Park, TN	F	R[c]	302	SO		36.0	85.7
MCK	Mackville, KY	A	R	353	SO	SR	37.7	85.0
PAR	Parsons, WV	F	C[c]	510	SO	SR	39.1	79.7
PED	Prince Edward, VA	F	R	146	SO		37.2	78.3
SHN	Big Meadows, VA	F	M	1073	SO	HE	38.5	78.4
SND	Sand Mountain, AL	A	R	352	SO		34.3	86.0
SPD	Speedwell, TN	A	R	361	SO		36.5	83.8
SUM	Sumatra, FL	F	FL	14	SO	BKG	30.1	85.0
VPI	Horton Station, VA	A	M[c]	920	SO	HE	37.3	80.6

[a] Land use category within 10 km of site: A, agricultural; F, forested; S, suburban.

[b] Terrain classification (local ground slope): FL, flat (< 5°); R, rolling (5–15°); C, complex (> 15°); M, montane.

[c] Assumptions for applying the multilayer model (MLM) may not be satisfied.

[d] Geographical regions: MW, midwest; NE, northeast; SO, south; individual sites are identified by region in the same order shown in Figs. 5–8.

[e] Special category sites: BKG, background; HE, high elevation; SR, source region.

In SS07b temporal changes in air quality and deposition in the eastern states between the early 1990s and early 2000s (i.e., P1-to-P3) were described and discussed. The record is expanded in the current paper to include a fourth 5-year period. Here, emphasis is on temporal changes occurring between the early 1990s and late 2000s (i.e., P1-to-P4) as new and continuing pollution controls have become mature and their impacts apparent. Results are displayed in a consistent manner to previous work (SS07a and b) to facilitate comparison. See Table 2 for definitions of terms and pollutant metrics used in the text, tables, and figures.

2 Approach

Monitoring data collected in the east between 1990 and 2009 at 34 CASTNET http://epa.gov/castnet/javaweb/index.html dry monitoring sites and paired NADP http://nadp.sws.uiuc.edu/ wet monitoring sites provide a sufficiently complete 20-year record to permit examination. Weekly concentrations of gaseous SO_2 and nitric acid (HNO_3), and aerosol sulfate (SO_4), nitrate (NO_3), and ammonium (NH_4) (using 3-stage filter packs) and hourly concentrations of O_3 (using continuous monitors) are determined at 10 m. Dry deposition of airborne species is estimated using the infer-

Table 2. Notation.

BKG	background
C	concentration
CV	coefficient of variation (100 SD$/(\overline{x})$)
CASTNET PM	sum of aerosol SO_4, NO_3, and NH_4 concentrations in total mass units
D	deposition
Dry HNO_3	dry deposition of monitored oxidized nitrogen from HNO_3, computed as ($14 \times HNO_3$ deposition/63), in units of mass of nitrogen
Dry N	dry deposition of nitrogen from HNO_3, aerosol NO_3, and aerosol NH_4, computed as (Dry OxN + Dry NH_4)
Dry NH_4	dry deposition of monitored reduced nitrogen from aerosol NH_4, computed as ($14 \times$ dry NH_4^+ ion deposition/18), in units of mass of nitrogen
Dry NO_3	dry deposition of monitored oxidized nitrogen from aerosol NO_3, computed as ($14 \times$ dry NO_3^- ion deposition/62), in units of mass of nitrogen
Dry O_3	dry deposition of ozone, in units of mass of O_3
Dry OxN	dry deposition of monitored oxidized nitrogen from HNO_3 and aerosol NO_3, computed as (Dry HNO_3 + Dry NO_3)
Dry S	dry deposition of oxidized sulfur from SO_2 and aerosol SO_4, computed as (Dry SO_2 + Dry SO_4)
Dry SO_2	dry deposition of oxidized sulfur from SO_2, computed as ($32 \times SO_2$ deposition/64), in units of mass of sulfur
Dry SO_4	dry deposition of oxidized sulfur from aerosol SO_4, computed as ($32 \times$ dry SO_4^{2-} ion deposition/96), in units of mass of sulfur
(D/T) N	ratio of dry N deposition to total N deposition, computed as Dry N/Total N
(D/T) NH_4	ratio of dry NH_4 deposition to total (dry plus wet) NH_4 deposition, computed as Dry NH_4/Total NH_4
(D/T) OxN	ratio of dry OxN deposition to total (dry plus wet) OxN deposition, computed as Dry OxN/Total OxN
(D/T) S	ratio of dry S deposition to total (dry plus wet) S deposition, computed as Dry S/Total S
E	eastern US
F	fall (Sep, Oct, Nov)
HE	high elevation
HNO_3	nitric acid (HNO_3) concentration
MW	midwest
n	number of site-specific period values comprising the mean
N	monitored oxidized plus reduced nitrogen, present as HNO_3, aerosol NO_3 and aerosol NH_4, in units of mass of nitrogen
NE	northeast
NH_4	ammonium (NH_4^+) ion concentration
NI	neutralization index, computed as $[(NH_4/18) - (NO_3/62)]/2(SO_4/96)$, using airborne concentrations in molar units
NO_3	nitrate (NO_3^-) ion concentration
O_3	ozone (O_3) concentration, in ppb
OA	over all, i.e., period–site means averaged over sites ≈ annual average for 5 yr period
OxN	monitored oxidized nitrogen present as HNO_3 and aerosol NO_3, computed as $(14 \times HNO_3/63) + (14 \times NO_3/62)$, in units of mass of nitrogen
PR	precipitation rate, in units of $cm\,yr^{-1}$ or $cm\,season^{-1}$
RFHNO_3	ratio of dry HNO_3 deposition to dry OxN deposition, computed as Dry HNO_3/Dry OxN
RFSO_2	ratio of dry SO_2 deposition to dry S deposition, computed as Dry SO_2/Dry S
RHNO_3	ratio of oxidized nitrogen concentration from HNO_3 to oxidized nitrogen present as OxN, computed as $(14 \times HNO_3/63)/OxN$
RNFHNO_3	ratio of dry HNO_3 deposition to dry N deposition, computed as Dry HNO_3/Dry N
RNFNH_4	ratio of dry NH_4 deposition to dry N deposition, computed as Dry NH_4/Dry N
RNHNO_3	ratio of oxidized nitrogen concentration from HNO_3 to nitrogen present as N, computed as $(14 \times HNO_3/63)/N$
RNNH_4	ratio of reduced nitrogen concentration from aerosol NH_4 to nitrogen present as N, computed as $(14 \times NH_4/18)/N$
RNO_3	ratio of oxidized nitrogen concentration from aerosol NO_3 to oxidized nitrogen present as OxN, computed as $(14 \times NO_3/62)/OxN$, also as $1 - RHNO_3$
RSO_2	ratio of airborne oxidized sulfur concentration from SO_2 to airborne oxidized sulfur present S, computed as $(32 \times SO_2/64)/S$
S	monitored oxidized sulfur present as SO_2 and aerosol SO_4, computed as $(32 \times SO_2/64) + (32 \times SO_4/96)$, in units of mass of sulfur
SO	south
SO_2	sulfur dioxide (SO_2) concentration
SO_4	sulfate (SO_4^{2-}) ion concentration
Sp	spring (Mar, Apr, May)
SR	source region
Su	summer (Jun, Jul, Aug)
Total N	sum of total dry plus wet deposition of monitored nitrogen, computed as (Dry N + Wet N)
Total NH_4	sum of dry plus wet deposition of monitored reduced nitrogen, computed as (Dry NH_4 + Wet NH_4), in units of mass of nitrogen
Total OxN	sum of dry plus wet deposition of monitored oxidized nitrogen, computed as (Dry OxN + Wet OxN), in units of mass of nitrogen
Total S	total dry plus wet oxidized sulfur deposition, computed as (Dry S + Wet S), in units of mass of sulfur
W	winter (Dec, Jan, Feb)
Wet H^+	wet deposition of aqueous H^+ ion, in units of mass of hydrogen
Wet N	wet deposition of nitrogen from aqueous NO_3^- ion and aqueous NH_4^+ ion, computed as (Wet OxN + Wet NH_4)
Wet NH_4	wet deposition of reduced nitrogen from aqueous NH_4^+ ion, computed as ($14 \times$ aqueous NH_4^+ ion deposition/18), in units of mass of nitrogen
Wet OxN	wet deposition of oxidized nitrogen from aqueous NO_3^- ion, computed as ($14 \times$ aqueous NO_3^- ion deposition/62), in units of mass of nitrogen
Wet S	wet deposition of oxidized sulfur from aqueous SO_4^{2-} ion, computed as ($32 \times$ aqueous SO_4^{2-} ion deposition/96), in units of mass of sulfur

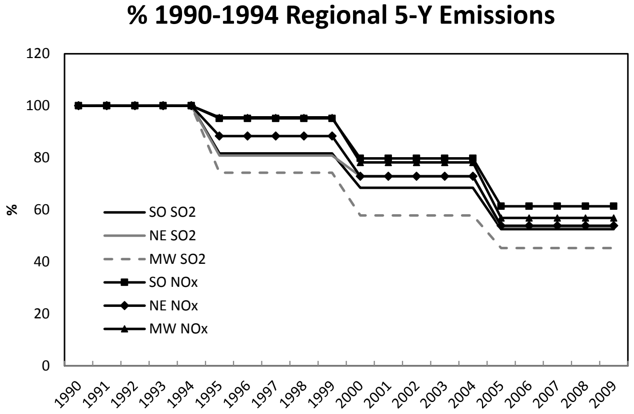


Figure 3. Estimates of regional mean annual SO_2 and NO_x emissions for four 5-year periods (P1, P2, P3, and P4) between 1990 and 2009, expressed as percentages of the 1990–1994 (P1) regional means. In the SO, NE, and MW mean P1 SO_2 emissions are 3.48, 1.68, and 3.27 $Tg\,S\,yr^{-1}$, and mean P1 NO_x emissions are 1.89, 1.06, and 1.35 $Tg\,N\,yr^{-1}$ (Xing et al., 2013).

ential model by multiplying modeled deposition velocities (Vd) by the monitored atmospheric concentration for the gas or aerosol species of interest. Deposition velocities for gases and aerosols are estimated using the multilayer model (MLM) (Meyers et al., 1998; Wesely et al., 1985). Monitoring data are composed from reported weekly (hourly for O_3) measurements into estimates of means for year, site, and season. These year–site–season means, computed for atmospheric concentration, Vd, precipitation rate (PR), and dry, wet, and total deposition, are averaged to period–site–season means and used to examine differences between 5-year periods for seasons, sites, and predefined groupings of sites. The data, methodologies, data quality (i.e., precision and accuracy), covariance of concentration and Vd, impacts of nonideal landscape features, adjustments for sampling artifacts, and data completeness criteria for accepting mean estimates of measurement data are described in SS07a.

Monitoring site locations, 10 in the MW and NE, and 14 in the SO, are identified in Fig. 2 and Table 1. These 34 sites provide sparse coverage, especially in the southern part of the SO and the northeastern part of the NE. Three additional environmental groupings of monitoring sites are also defined as subsets of the eastern sites: background (BKG), high elevation (HE), and SR. These sites are chosen to reveal distinctions in pollutant behavior characteristic of their environments (Table 1 and SS07a).

CASTNET monitoring locations were initially sited to avoid the influence of major cities, highways, local activities, and point and area sources of pollutants and to be regionally representative (i.e., similar to a characteristic 80 by 80 km area surrounding the site) (Clarke et al., 1997; Baumgardner et al., 2002). In the current study, most of the CASTNET sites are located within 50 km of a paired NADP–NTN (National Trends Network) wet deposition site.

Collocated precision estimates (as CVs) of weekly CASTNET concentration, Vd, and dry deposition at eastern sites are within 5 to 10 % for the major species (Clarke et al., 1997; Sickles and Shadwick, 2002). Corresponding precision estimates are 5 % for weekly NADP PR, wet S (i.e., wet deposition of sulfate; see Table 2), and wet OxN; 10 % for wet H^+; and 15 % for wet NH_4 (Nilles et al., 1994). These estimates for weekly network results are likely to be conservative for corresponding longer-duration 5-year period results.

Total oxidized nitrogen (NO_y) includes the primary NO_x species (NO and NO_2) plus the secondary species (HNO_3, nitrous acid (HNO_2), aerosol NO_3, peroxyacetylnitrate (PAN), as well as other oxidized organic nitrogen species). Total reduced nitrogen (NH_x) includes both gaseous ammonia (NH_3) and aerosol NH_4. In the current study, only two of the NO_y species, HNO_3 and aerosol NO_3, (their sum is OxN), and only one of the NH_x species, aerosol NH_4, are monitored. As a result, reported estimates of dry deposition of OxN and NH_4 underestimate corresponding values for NO_y and NO_x.

The contribution of coarse (i.e., > 2.5 µm) particles to total particulate deposition likely depends on location and proximity to sources of crustal dusts, road salt, and marine aerosols. Since the contribution of coarse particles is ignored in the MLM, where all particles are modeled as fine aerosol SO_4 particles, current estimates of particulate dry deposition are biased low. However, the non-size selective CASTNET filter pack sampler likely over-samples the fine tail of coarse particle distribution. Although this may not be too important for aerosol SO_4 and NH_4, which occur mainly as fine particles, it would underestimate the contribution of dry deposition of aerosol NO_3, where appreciable coarse aerosol NO_3 can occur (Wolff, 1984; Lefer and Talbot, 2001).

As noted in SS07a (and references therein), use of the CASTNET filter pack sampler introduces sampling artifacts, especially to nitrogen-containing species. Findings from Sickles and Shadwick (2008), as well as wind tunnel and modeling studies (unpublished) of particle sampling characteristics of the non-size selective open-faced CASTNET filter pack inside its weather shield over a range of wind speeds, suggest appreciable collection of both fine (< 2.5 µm) and coarse particles on the first filter (Teflon) of the filter pack. Although both aerosol SO_4 and NH_4 exist mainly in the fine fraction (< 1 µm) year round, aerosol NO_3 is multi-modal, and in non-marine environments exists mainly (>75 %) in the fine fraction in cool seasons and mainly as larger (>4 µm) particles during warm seasons (Wolff, 1984; Lefer and Talbot, 2001; Zhang et al., 2008; Lee et al., 2008). Sampling artifacts in opposing directions may arise through possible loss of aerosol NH_4NO_3 during sampling and by aspiration of the fine tail of coarse aerosol NO_3. Aerosol NH_4NO_3 (nominally < 2.5 µm) collected on the Teflon filter may be lost during sampling by volatilization into gaseous HNO_3 and NH_3, driven by departures from equilibrium (exaggerated at higher temperatures) and/or by reaction with strong acids. Results from comparison studies (Sickles and Shadwick, 2002, 2008; Lee et al., 2008; Zhang et al., 2009) are consistent with loss of NH_4NO_3 from the Teflon filter followed by collection of volatilized HNO_3 on the downstream nylon filter of the CASTNET filter pack during warm season sampling and with minimal volatilization loss during cool season sampling. Coarse alkaline particles (e.g., sea/road salt or soil/mineral dust) may contain aerosol NO_3 (possibly formed by scavenging HNO_3 while airborne), and to the extent that they are collected, these larger particles may provide a high bias to CASTNET aerosol NO_3 relative to its fine ($PM_{2.5}$) contribution. Some of these larger particles (if unreacted and retained on the Teflon filter) may scavenge airborne HNO_3 from sampled air during week-long sampling periods, also providing a high bias to aerosol NO_3 and a low bias to HNO_3.

Some of these concepts are illustrated by the performance of Interagency Monitoring of Protected Visual Environments (IMPROVE) samplers with 2.5 µm size selective inlet and CASTNET samplers collocated at 10 eastern monitoring sites (Sickles and Shadwick, 2008). At the eight non-marine sites good agreement was found for aerosol SO_4 (CASTNET was biased high by 4 to 7 %), and more variability was found for aerosol NO_3 (CASTNET ranged between 25 % higher and 39 % lower). Seasonally, aerosol NO_3 showed median relative biases ranging between 5 and −10 % for all seasons, except summer, where the IMPROVE aerosol NO_3 exceeded the corresponding CASTNET values by > 40 % (this was at very low concentrations where the median bias was $0.07\,\mu g\,m^{-3}$). Finally, although CASTNET and IMPROVE aerosol NO_3 displayed mixed comparisons at eight inland sites, CASTNET sites showed consistently higher aerosol NO_3 (40–100 %) at the two marine-influenced sites, which was attributed to over-sampling the fine tail of coarse sea salt aerosols by the CASTNET sampler.

Thus, in the current study, minimal CASTNET sampling bias is expected for aerosol SO_4 and NH_4, which occur mainly as fine particles. However, HNO_3 and aerosol NO_3 as well as other metrics derived from them are subject to sampling biases that act in opposing directions. Volatilization of collected NH_4NO_3 during sampling could lead to a high bias of HNO_3 and a low bias of aerosol NO_3. In contrast, the non-size selective sampler inlet could lead to an over-sampling of the fine tail of coarse aerosol NO_3 with a high bias of aerosol NO_3 and a potentially low bias of HNO_3. The impacts of these biases are expected to be minimal during cool season sampling at non-marine sites. As a result, in the current study HNO_3, aerosol NO_3, and metrics derived from them (e.g., CASTNET PM, Dry HNO_3, Dry NO_3, RNO_3 and other ratios of concentration and deposition) should be viewed with caution, especially during summer.

Uncertainties in Vd, rather than concentration, likely limit the accuracy of dry deposition estimates (Hicks et al., 1991; Lovett and Lindberg, 1993). Accuracy of Vd estimates has not been well established. Based on comparisons with field measurements, the MLM may provide fairly accurate estimates of Vd for SO_2, O_3, and HNO_3 to many surfaces (e.g., crops; Meyers et al., 1998); however, Vd for SO_2 to forested canopies may be underestimated by ≈ 35 % (Finkelstein et al., 2000). Recent comparison at the same site of weekly CASTNET MLM Vd estimates with those from a similar model used by the Canadian Air and Precipitation Monitoring Network (CAPMoN) shows CASTNET Vd to be low (relative to CAPMoN) by approximately 50 % for SO_2 and 35 % for HNO_3; differences of hourly estimates between the two models could be as large as a factor of 2–3 (Schwede et al., 2011). Annual average small-scale spatial variability (0.5 km) of model-estimated Vd was estimated at 10 % for SO_2 and O_3, 30 % for aerosol SO_4, and 40 % for HNO_3 (Brook et al., 1997). Uncertainty of the inferential model has been estimated at 25 % for O_3, 30 % for SO_2 and ≥40 % for HNO_3 and particles (Clarke et al., 1997). These estimates may be appropriate for areas with ideal terrain and uniform land use; however, non-ideal landscape features (e.g., irregular terrain and/or forested canopies) likely contribute low biases to concentration, estimated Vd, and dry deposition estimates, and increase their resulting uncertainty (Clarke et al., 1997; Hicks, 2006). The distribution of influential landscape features across sites suggests that their impacts result in the greatest underestimates at sites in the south and northeast geographical regions, and that their impacts should be smaller at sites in the midwestern grouping. Much of the above evidence suggests that CASTNET Vd estimates, while uncertain, likely provide conservative lower bound estimates of dry deposition.

Internetwork comparisons of annual wet deposition have been conducted for the periods 1986–1993 (Sirois et al., 2000) and 1995–2004 (Wetherbee et al., 2010) at collocated NADP and CAPMoN sites. NADP results for precipitation depth and wet deposition of H^+, NH_4, S, and OxN appear to be biased low relative to CAPMoN by less than 30 %. Although there are no standards for determining accuracy, current NADP results are possibly biased low and likely accurate within 25 %.

The east has large heterogeneities in its spatial distribution of land cover (i.e., crops, forests, and suburban), of terrain (i.e., flat, rolling, complex, and montane) and of pollution sources (e.g., EGU sources in the Ohio Valley and mobile sources in urban centers). As a result, it is unlikely that the sparse coverage of CASTNET (i.e., 34 sites) can provide truly accurate regional representations. This is supported by a recent modeling study of wet deposition (Sickles et al., 2009) where current study site locations were found to over represent geographical areas subject to both high emissions and wet deposition, yielding over-estimations of corresponding regional values by 5 to 25 %. Nevertheless, for the current study, values representing areas with common geographical and environmental characteristics are approximated as the means of values from sites associated with each classification. It is assumed that these estimates are useful as rough indices of their respective geographical regions and environmental groupings.

As indicated above, the airborne concentration, estimated Vd, and dry and wet deposition estimates may be subject to sizeable uncertainties. However, assuming constant bias, their precision to a first approximation is expected to control the uncertainty associated with the current examination of period-to-period (e.g., P1-to-P4) temporal changes.

Data have been composed from reported measurements into estimates of means for year, site, and season. Year–site–season means were computed for atmospheric concentration, Vd, PR, and dry, wet, and total deposition. Consistent with previous work (SS07a and b) these values, averaged to period–site–season means, are used to examine differences between 5-year emission periods for seasons, sites, and predefined site groupings. Seasons (e.g., data for winter, W, 1990 include data from December 1989 through February 1990; spring, Sp; summer, Su; and fall, F) are used to define the years in periods. Five-year periods have been chosen to coincide with emission patterns (noted earlier), to minimize the impacts of missing data on seasonal means, to reduce the impact of meteorological variability, and to maintain consistency with earlier studies. For example, Table 3 presents averages of year–site–season means averaged over all the years in P4 and all the sites in each specified site grouping. Analogous tabulations for P1, P2, and P3 may be found in SS07a and b.

The approach to data analysis, described in detail in SS07b, uses mean squared error derived from analysis of variance of mean estimates for each pollutant metric to examine period-to-period differences in the monitoring data and metrics derived from them. Use of the term significant implies comparison where a statistical test is satisfied at the $p = 0.05$ significance level, and NS implies a non-significant test result ($p > 0.05$). Comparison with no mention of significance, using the term numerically implies nominal comparison where one comparator is numerically different from another, without statistical testing. The statistical tests that were performed apply only to absolute differences. Relative differences (changes) are used as a convenient construct to enable discussion of the absolute differences.

3 Results

Means of each species-specific value of P4 atmospheric concentration, Vd, PR, dry, wet, and total deposition, and selected ratios are presented in Table 3 for each site grouping. Corresponding across-site variabilities are given as coefficients of variation (CV). Results are displayed for each grouping of monitoring sites over all seasons and for the east by specific season. P1-to-P4 absolute changes in both native units and relative differences (%) are displayed in Fig. 4 for each geographical region. To facilitate identification of patterns of P1-to-P4 changes, significant ($p \leq 0.05$) decreases are colored blue, and increases are colored pink. Six sets of period-to-period differences are considered (e.g., P1-to-P2, P1-to-P3); however, they are not tabulated due to space limitations. Although not shown comprehensively, P3-to-P4 differences are discussed in a few instances to contrast with P1-to-P4 differences. Graphical illustrations of period-to-period comparisons of concentration, deposition, and related metrics as well as relative changes by site and region have been created for each of the entries shown in Table 3. Example illustrations for selected airborne concentration (i.e., S, OxN, N and CASTNET PM) and deposition (i.e., total S, total OxN, total N and wet H^+) are shown for all sites in Figs. 5 and 6.

3.1 Deposition velocity and precipitation rate

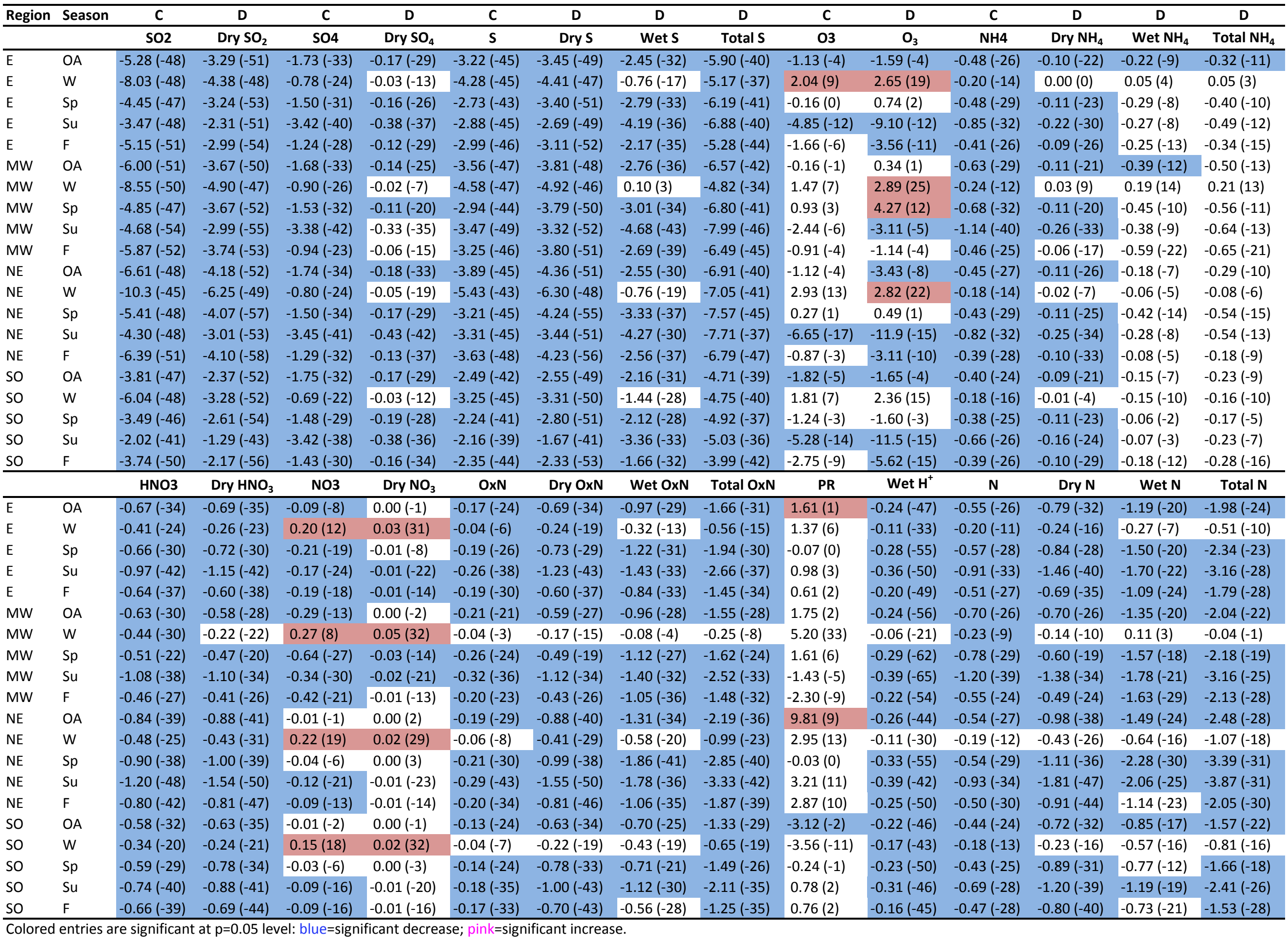
Deposition velocity and its analog, PR, may be viewed as velocities at which pollutants are delivered (i.e., deposited via dry and wet deposition) to the Earth's surface. Both Vd and PR are strongly influenced by meteorology. One of the reasons for selecting 5-year averaging periods in the current study is to reduce the confounding influences of year-to-year meteorological variability in assessing the impacts of changes in pollutant emissions on resulting ambient atmospheric concentrations, dry deposition, and wet deposition.

The variabilities of Vd and PR are fairly low. In the case of Vd, this is indicated by the 2010 CASTNET decision (http://epa.gov/castnet/javaweb/docs/CASTNET_Factsheet_2013.pdf) to discontinue meteorological monitoring and use site-specific historical average Vd at all but five monitoring sites (Bowker et al., 2011). In the current study, period–site–season-specific CVs, averaged across all periods, sites, and seasons for Vd for aerosol, O_3, SO_2, and HNO_3 are each < 5 %, and the corresponding value for PR is < 9 %. For the east and for each of the three geographic regions, entity-specific relative differences were determined for each of the six possible period-to-period comparisons (i.e., $4 \times 6 = 24$ relative differences per entity), yielding median absolute relative differences ≤ 6 % for Vd of each of the four species and PR. Similar comparisons at the site-specific level ($34 \times 6 = 204$ relative differences per entity) yield median absolute relative differences ≤ 7 % for Vd of each of the four species and PR.

Since period-to-period changes in Vd are usually small, the behavior of P1-to-P4 changes in species atmospheric concentration and dry deposition are generally similar, and the relative behavior of the dry deposition of a species is often mirrored by that of its airborne concentration. However, there are instances where opposing changes in Vd are sufficient to cause the resulting change in species deposition to differ appreciably and sometimes significantly from its corresponding atmospheric concentration. For example, wintertime increases in aerosol Vd yield changes in dry deposition that tend to moderate P1-to-P4 reductions apparent in atmo-

Table 3. Mean (CV) atmospheric concentration, deposition velocity, precipitation rate, dry, wet, and total deposition, and concentration and deposition metrics at 34 eastern US CASTNET and selected subsets of sites for the 5-year period 2005–2009 (see Table 2 for definitions).

	Site grouping										
Region	E					NE	MW	SO	SR	HE	BKG
season	OA	W	Sp	Su	F	OA	OA	OA	OA	OA	OA
n	34	34	34	34	34	10	10	14	15	3	4
2005–2009 Atmospheric concentration, $\mu g\,m^{-3}$											
SO_2	5.63 (51)	8.83 (55)	5.00 (47)	3.75 (54)	4.98 (52)	7.22 (49)	5.87 (41)	4.33 (48)	7.61 (28)	6.45 (27)	1.54 (16)
SO_4	3.52 (22)	2.49 (18)	3.33 (21)	5.13 (28)	3.12 (21)	3.32 (32)	3.41 (23)	3.74 (12)	3.94 (9)	3.49 (15)	2.32 (39)
S (as S)	4.00 (40)	5.25 (48)	3.61 (37)	3.59 (39)	3.53 (41)	4.72 (45)	4.08 (35)	3.42 (34)	5.12 (22)	4.39 (23)	1.55 (25)
HNO_3	1.32 (32)	1.26 (35)	1.56 (33)	1.35 (40)	1.12 (35)	1.33 (42)	1.46 (24)	1.22 (28)	1.51 (20)	1.55 (10)	0.68 (43)
NO_3	1.04 (64)	1.85 (72)	0.92 (68)	0.55 (36)	0.85 (69)	0.78 (50)	1.92 (17)	0.60 (48)	1.38 (52)	0.56 (25)	0.73 (83)
OxN (as N)	0.53 (40)	0.70 (41)	0.55 (41)	0.42 (35)	0.44 (44)	0.47 (43)	0.76 (15)	0.41 (30)	0.65 (31)	0.47 (1)	0.32 (49)
NH_4	1.35 (26)	1.20 (39)	1.20 (26)	1.80 (28)	1.19 (25)	1.23 (36)	1.56 (17)	1.28 (22)	1.58 (13)	1.22 (6)	0.78 (37)
N (as N)	1.58 (29)	1.63 (40)	1.49 (30)	1.82 (26)	1.36 (30)	1.43 (37)	1.97 (16)	1.40 (23)	1.88 (19)	1.42 (4)	0.92 (40)
O_3 (ppb)	30.8 (14)	24.6 (16)	38.4 (11)	34.5 (21)	25.6 (18)	30.3 (10)	30.6 (6)	31.4 (20)	30.4 (11)	39.4 (10)	28.0 (14)
Vd, $cm\,s^{-1}$											
HNO_3	1.16 (21)	0.96 (27)	1.31 (19)	1.35 (19)	1.04 (24)	1.13 (28)	1.23 (11)	1.13 (21)	1.19 (21)	1.29 (7)	1.14 (24)
SO_2	0.31 (29)	0.31 (40)	0.32 (30)	0.33 (22)	0.29 (32)	0.30 (30)	0.36 (21)	0.28 (32)	0.36 (22)	0.30 (9)	0.25 (27)
O_3	0.17 (17)	0.09 (18)	0.17 (24)	0.26 (20)	0.15 (18)	0.16 (18)	0.15 (15)	0.17 (17)	0.17 (17)	0.19 (9)	0.16 (19)
Aerosol	0.10 (21)	0.08 (28)	0.13 (19)	0.12 (22)	0.09 (24)	0.10 (28)	0.11 (12)	0.10 (22)	0.10 (22)	0.11 (15)	0.10 (18)
PR (cm/time)	119 (19)	25.7 (27)	30.3 (24)	32.7 (20)	29.6 (24)	119 (12)	100 (20)	132 (15)	115 (14)	126 (17)	124 (29)
Deposition, $kg\,(ha\,yr)^{-1}$											
Dry SO_2 (as S)	3.13 (62)	4.84 (70)	2.83 (61)	2.20 (58)	2.58 (62)	3.91 (60)	3.68 (51)	2.18 (61)	4.61 (35)	2.96 (14)	0.67 (12)
Dry SO_4 (as S)	0.40 (33)	0.21 (35)	0.46 (30)	0.63 (37)	0.29 (34)	0.36 (45)	0.40 (31)	0.42 (27)	0.44 (25)	0.43 (23)	0.23 (28)
Dry S (as S)	3.53 (58)	5.06 (68)	3.29 (55)	2.83 (51)	2.87 (58)	4.27 (58)	4.09 (48)	2.60 (55)	5.05 (33)	3.40 (14)	0.91 (13)
Wet S (as S)	5.22 (28)	3.59 (35)	5.65 (29)	7.53 (38)	3.97 (26)	5.96 (31)	4.97 (30)	4.86 (20)	6.25 (18)	5.13 (11)	3.16 (31)
Total S (as S)	8.75 (36)	8.65 (47)	8.93 (35)	10.4 (38)	6.84 (35)	10.2 (38)	9.06 (37)	7.47 (25)	11.3 (19)	8.53 (5)	4.06 (27)
Dry HNO_3 (as N)	1.28 (41)	0.89 (45)	1.65 (41)	1.60 (45)	0.98 (45)	1.24 (54)	1.48 (35)	1.16 (36)	1.48 (34)	1.46 (18)	0.62 (41)
Dry NO_3 (as N)	0.07 (66)	0.11 (73)	0.09 (68)	0.05 (48)	0.05 (75)	0.06 (67)	0.13 (21)	0.04 (62)	0.10 (56)	0.04 (20)	0.05 (86)
Dry OxN (as N)	1.35 (41)	1.00 (42)	1.74 (42)	1.65 (44)	1.03 (45)	1.30 (54)	1.61 (33)	1.21 (36)	1.58 (34)	1.50 (18)	0.66 (36)
Wet OxN (as N)	2.35 (19)	2.06 (28)	2.76 (22)	2.86 (22)	1.73 (23)	2.56 (24)	2.45 (15)	2.14 (11)	2.67 (12)	2.17 (17)	1.78 (26)
Total OxN (as N)	3.71 (22)	3.06 (25)	4.50 (25)	4.51 (25)	2.76 (24)	3.86 (29)	4.06 (19)	3.35 (13)	4.25 (14)	3.67 (5)	2.45 (28)
Dry NH_4 (as N)	0.35 (38)	0.24 (49)	0.38 (35)	0.52 (38)	0.26 (39)	0.31 (51)	0.41 (26)	0.34 (37)	0.41 (30)	0.35 (19)	0.18 (32)
Wet NH_4 (as N)	2.30 (27)	1.29 (33)	3.14 (35)	3.10 (31)	1.65 (34)	2.23 (29)	2.87 (21)	1.94 (14)	2.64 (22)	2.33 (25)	1.79 (54)
Total NH_4 (as N)	2.65 (26)	1.53 (32)	3.53 (33)	3.62 (28)	1.91 (31)	2.54 (29)	3.28 (19)	2.28 (15)	3.05 (21)	2.68 (20)	1.97 (52)
Dry N (as N)	1.70 (40)	1.24 (40)	2.12 (40)	2.17 (41)	1.29 (43)	1.61 (53)	2.02 (31)	1.54 (35)	1.98 (33)	1.85 (18)	0.85 (32)
Wet N (as N)	4.66 (21)	3.36 (26)	5.90 (27)	5.96 (24)	3.38 (26)	4.79 (25)	5.32 (17)	4.08 (11)	5.32 (14)	4.50 (21)	3.58 (37)
Total N (as N)	6.36 (22)	4.59 (24)	8.02 (26)	8.13 (25)	4.67 (24)	6.41 (28)	7.34 (16)	5.63 (13)	7.30 (15)	6.35 (11)	4.42 (34)
Wet H^+	0.26 (37)	0.23 (34)	0.23 (38)	0.37 (49)	0.21 (34)	0.34 (31)	0.20 (41)	0.25 (25)	0.31 (33)	0.26 (8)	0.15 (50)
Dry O_3	39.5 (27)	16.3 (28)	48.3 (29)	66.1 (33)	28.5 (31)	38.3 (28)	36.6 (18)	42.3 (30)	40.4 (25)	56.4 (10)	32.3 (18)
Concentration and deposition metrics											
RSO_2	0.67 (16)	0.81 (11)	0.66 (16)	0.49 (23)	0.66 (17)	0.73 (12)	0.71 (7)	0.60 (18)	0.73 (7)	0.73 (5)	0.51 (17)
$RFSO_2$	0.85 (9)	0.93 (5)	0.82 (12)	0.74 (14)	0.86 (9)	0.89 (6)	0.88 (7)	0.80 (11)	0.91 (3)	0.87 (3)	0.75 (7)
(D/T) S	0.37 (33)	0.53 (33)	0.35 (32)	0.27 (36)	0.39 (34)	0.38 (37)	0.43 (20)	0.33 (38)	0.44 (20)	0.40 (14)	0.23 (19)
NI	0.79 (10)	0.70 (13)	0.75 (12)	0.85 (10)	0.80 (9)	0.80 (8)	0.78 (6)	0.78 (13)	0.80 (7)	0.81 (5)	0.67 (22)
$RHNO_3$	0.59 (22)	0.47 (43)	0.65 (19)	0.69 (12)	0.60 (23)	0.62 (12)	0.42 (18)	0.68 (12)	0.55 (23)	0.73 (9)	0.51 (33)
RNO_3	0.41 (32)	0.53 (37)	0.35 (36)	0.31 (28)	0.40 (35)	0.38 (21)	0.58 (13)	0.32 (24)	0.45 (29)	0.27 (26)	0.49 (34)
$RNHNO_3$	0.19 (18)	0.20 (44)	0.23 (17)	0.16 (27)	0.18 (22)	0.20 (18)	0.16 (15)	0.19 (17)	0.18 (15)	0.24 (6)	0.17 (26)
$RNNH_4$	0.67 (8)	0.58 (6)	0.64 (9)	0.76 (8)	0.69 (10)	0.68 (6)	0.61 (2)	0.71 (6)	0.66 (8)	0.67 (2)	0.66 (6)
$RFHNO_3$	0.95 (3)	0.89 (11)	0.95 (3)	0.97 (2)	0.95 (3)	0.96 (2)	0.91 (4)	0.96 (1)	0.94 (3)	0.97 (1)	0.92 (7)
$RNFHNO_3$	0.75 (6)	0.72 (18)	0.77 (7)	0.73 (8)	0.75 (7)	0.76 (5)	0.72 (7)	0.75 (5)	0.75 (4)	0.79 (1)	0.72 (14)
$RNFNH_4$	0.21 (15)	0.19 (35)	0.19 (21)	0.25 (22)	0.21 (22)	0.20 (17)	0.21 (15)	0.22 (15)	0.21 (10)	0.19 (2)	0.22 (25)
(D/T) OxN	0.35 (28)	0.32 (31)	0.37 (27)	0.35 (30)	0.36 (32)	0.32 (38)	0.39 (18)	0.35 (27)	0.36 (25)	0.41 (19)	0.27 (12)
(D/T) NH_4	0.13 (32)	0.16 (39)	0.11 (34)	0.15 (39)	0.14 (38)	0.12 (39)	0.13 (29)	0.15 (30)	0.13 (28)	0.14 (31)	0.10 (18)
(D/T) N	0.26 (29)	0.27 (32)	0.26 (30)	0.26 (31)	0.27 (34)	0.24 (38)	0.27 (25)	0.27 (27)	0.27 (26)	0.30 (25)	0.19 (17)
CASTNET PM	5.91 (24)	5.55 (36)	5.45 (24)	7.49 (26)	5.16 (25)	5.33 (34)	6.89 (17)	5.62 (16)	6.90 (13)	5.28 (9)	3.83 (32)



Region	Season	C	D	C	D	C	D	D	D	C	D	C	D	D	D
		SO2	Dry SO_2	SO4	Dry SO_4	S	Dry S	Wet S	Total S	O3	O_3	NH4	Dry NH_4	Wet NH_4	Total NH_4
E	OA	-5.28 (-48)	-3.29 (-51)	-1.73 (-33)	-0.17 (-29)	-3.22 (-45)	-3.45 (-49)	-2.45 (-32)	-5.90 (-40)	-1.13 (-4)	-1.59 (-4)	-0.48 (-26)	-0.10 (-22)	-0.22 (-9)	-0.32 (-11)
E	W	-8.03 (-48)	-4.38 (-48)	-0.78 (-24)	-0.03 (-13)	-4.28 (-45)	-4.41 (-47)	-0.76 (-17)	-5.17 (-37)	2.04 (9)	2.65 (19)	-0.20 (-14)	0.00 (0)	0.05 (4)	0.05 (3)
E	Sp	-4.45 (-47)	-3.24 (-53)	-1.50 (-31)	-0.16 (-26)	-2.73 (-43)	-3.40 (-51)	-2.79 (-33)	-6.19 (-41)	-0.16 (0)	0.74 (2)	-0.48 (-29)	-0.11 (-23)	-0.29 (-8)	-0.40 (-10)
E	Su	-3.47 (-48)	-2.31 (-51)	-3.42 (-40)	-0.38 (-37)	-2.88 (-45)	-2.69 (-49)	-4.19 (-36)	-6.88 (-40)	-4.85 (-12)	-9.10 (-12)	-0.85 (-32)	-0.22 (-30)	-0.27 (-8)	-0.49 (-12)
E	F	-5.15 (-51)	-2.99 (-54)	-1.24 (-28)	-0.12 (-29)	-2.99 (-46)	-3.11 (-52)	-2.17 (-35)	-5.28 (-44)	-1.66 (-6)	-3.56 (-11)	-0.41 (-26)	-0.09 (-26)	-0.25 (-13)	-0.34 (-15)
MW	OA	-6.00 (-51)	-3.67 (-50)	-1.68 (-33)	-0.14 (-25)	-3.56 (-47)	-3.81 (-48)	-2.76 (-36)	-6.57 (-42)	-0.16 (-1)	0.34 (1)	-0.63 (-29)	-0.11 (-21)	-0.39 (-12)	-0.50 (-13)
MW	W	-8.55 (-50)	-4.90 (-47)	-0.90 (-26)	-0.02 (-7)	-4.58 (-47)	-4.92 (-46)	0.10 (3)	-4.82 (-34)	1.47 (7)	2.89 (25)	-0.24 (-12)	0.03 (9)	0.19 (14)	0.21 (13)
MW	Sp	-4.85 (-47)	-3.67 (-52)	-1.53 (-32)	-0.11 (-20)	-2.94 (-44)	-3.79 (-50)	-3.01 (-34)	-6.80 (-41)	0.93 (3)	4.27 (12)	-0.68 (-32)	-0.11 (-20)	-0.45 (-10)	-0.56 (-11)
MW	Su	-4.68 (-54)	-2.99 (-55)	-3.38 (-42)	-0.33 (-35)	-3.47 (-49)	-3.32 (-52)	-4.68 (-43)	-7.99 (-46)	-2.44 (-6)	-3.11 (-5)	-1.14 (-40)	-0.26 (-33)	-0.38 (-9)	-0.64 (-13)
MW	F	-5.87 (-52)	-3.74 (-53)	-0.94 (-23)	-0.06 (-15)	-3.25 (-46)	-3.80 (-51)	-2.69 (-39)	-6.49 (-45)	-0.91 (-4)	-1.14 (-4)	-0.46 (-25)	-0.06 (-17)	-0.59 (-22)	-0.65 (-21)
NE	OA	-6.61 (-48)	-4.18 (-52)	-1.74 (-34)	-0.18 (-33)	-3.89 (-45)	-4.36 (-51)	-2.55 (-30)	-6.91 (-40)	-1.12 (-4)	-3.43 (-8)	-0.45 (-27)	-0.11 (-26)	-0.18 (-7)	-0.29 (-10)
NE	W	-10.3 (-45)	-6.25 (-49)	-0.80 (-24)	-0.05 (-19)	-5.43 (-43)	-6.30 (-48)	-0.76 (-19)	-7.05 (-41)	2.93 (13)	2.82 (22)	-0.18 (-14)	-0.02 (-7)	-0.06 (-5)	-0.08 (-6)
NE	Sp	-5.41 (-48)	-4.07 (-57)	-1.50 (-34)	-0.17 (-29)	-3.21 (-45)	-4.24 (-55)	-3.33 (-37)	-7.57 (-45)	0.27 (1)	0.49 (1)	-0.43 (-29)	-0.11 (-25)	-0.42 (-14)	-0.54 (-15)
NE	Su	-4.30 (-48)	-3.01 (-53)	-3.45 (-41)	-0.43 (-42)	-3.31 (-45)	-3.44 (-51)	-4.27 (-30)	-7.71 (-37)	-6.65 (-17)	-11.9 (-15)	-0.82 (-32)	-0.25 (-34)	-0.28 (-8)	-0.54 (-13)
NE	F	-6.39 (-51)	-4.10 (-58)	-1.29 (-32)	-0.13 (-37)	-3.63 (-48)	-4.23 (-56)	-2.56 (-37)	-6.79 (-47)	-0.87 (-3)	-3.11 (-10)	-0.39 (-28)	-0.10 (-33)	-0.08 (-5)	-0.18 (-9)
SO	OA	-3.81 (-47)	-2.37 (-52)	-1.75 (-32)	-0.17 (-29)	-2.49 (-42)	-2.55 (-49)	-2.16 (-31)	-4.71 (-39)	-1.82 (-5)	-1.65 (-4)	-0.40 (-24)	-0.09 (-21)	-0.15 (-7)	-0.23 (-9)
SO	W	-6.04 (-48)	-3.28 (-52)	-0.69 (-22)	-0.03 (-12)	-3.25 (-45)	-3.31 (-50)	-1.44 (-28)	-4.75 (-40)	1.81 (7)	2.36 (15)	-0.18 (-16)	-0.01 (-4)	-0.15 (-10)	-0.16 (-10)
SO	Sp	-3.49 (-46)	-2.61 (-54)	-1.48 (-29)	-0.19 (-28)	-2.24 (-41)	-2.80 (-51)	-2.12 (-28)	-4.92 (-37)	-1.24 (-3)	-1.60 (-3)	-0.38 (-25)	-0.11 (-23)	-0.06 (-2)	-0.17 (-5)
SO	Su	-2.02 (-41)	-1.29 (-43)	-3.42 (-38)	-0.38 (-36)	-2.16 (-39)	-1.67 (-41)	-3.36 (-33)	-5.03 (-36)	-5.28 (-14)	-11.5 (-15)	-0.66 (-26)	-0.16 (-24)	-0.07 (-3)	-0.23 (-7)
SO	F	-3.74 (-50)	-2.17 (-56)	-1.43 (-30)	-0.16 (-34)	-2.35 (-44)	-2.33 (-53)	-1.66 (-32)	-3.99 (-42)	-2.75 (-9)	-5.62 (-15)	-0.39 (-26)	-0.10 (-29)	-0.18 (-12)	-0.28 (-16)
		HNO3	Dry HNO_3	NO3	Dry NO_3	OxN	Dry OxN	Wet OxN	Total OxN	PR	Wet H^+	N	Dry N	Wet N	Total N
E	OA	-0.67 (-34)	-0.69 (-35)	-0.09 (-8)	0.00 (-1)	-0.17 (-24)	-0.69 (-34)	-0.97 (-29)	-1.66 (-31)	1.61 (1)	-0.24 (-47)	-0.55 (-26)	-0.79 (-32)	-1.19 (-20)	-1.98 (-24)
E	W	-0.41 (-24)	-0.26 (-23)	0.20 (12)	0.03 (31)	-0.04 (-6)	-0.24 (-19)	-0.32 (-13)	-0.56 (-15)	1.37 (6)	-0.11 (-33)	-0.20 (-11)	-0.24 (-16)	-0.27 (-7)	-0.51 (-10)
E	Sp	-0.66 (-30)	-0.72 (-30)	-0.21 (-19)	-0.01 (-8)	-0.19 (-26)	-0.73 (-29)	-1.22 (-31)	-1.94 (-30)	-0.07 (0)	-0.28 (-55)	-0.57 (-28)	-0.84 (-28)	-1.50 (-20)	-2.34 (-23)
E	Su	-0.97 (-42)	-1.15 (-42)	-0.17 (-24)	-0.01 (-22)	-0.26 (-38)	-1.23 (-43)	-1.43 (-33)	-2.66 (-37)	0.98 (3)	-0.36 (-50)	-0.91 (-33)	-1.46 (-40)	-1.70 (-22)	-3.16 (-28)
E	F	-0.64 (-37)	-0.60 (-38)	-0.19 (-18)	-0.01 (-14)	-0.19 (-30)	-0.60 (-37)	-0.84 (-33)	-1.45 (-34)	0.61 (2)	-0.20 (-49)	-0.51 (-27)	-0.69 (-35)	-1.09 (-24)	-1.79 (-28)
MW	OA	-0.63 (-30)	-0.58 (-28)	-0.29 (-13)	0.00 (-2)	-0.21 (-21)	-0.59 (-27)	-0.96 (-28)	-1.55 (-28)	1.75 (2)	-0.24 (-56)	-0.70 (-26)	-0.70 (-26)	-1.35 (-20)	-2.04 (-22)
MW	W	-0.44 (-30)	-0.22 (-22)	0.27 (8)	0.05 (32)	-0.04 (-3)	-0.17 (-15)	-0.08 (-4)	-0.25 (-8)	5.20 (33)	-0.06 (-21)	-0.23 (-9)	-0.14 (-10)	0.11 (3)	-0.04 (-1)
MW	Sp	-0.51 (-22)	-0.47 (-20)	-0.64 (-27)	-0.03 (-14)	-0.26 (-24)	-0.49 (-19)	-1.12 (-27)	-1.62 (-24)	1.61 (6)	-0.29 (-62)	-0.78 (-29)	-0.60 (-19)	-1.57 (-18)	-2.18 (-19)
MW	Su	-1.08 (-38)	-1.10 (-34)	-0.34 (-30)	-0.02 (-21)	-0.32 (-36)	-1.12 (-34)	-1.40 (-32)	-2.52 (-33)	-1.43 (-5)	-0.39 (-65)	-1.20 (-39)	-1.38 (-34)	-1.78 (-21)	-3.16 (-25)
MW	F	-0.46 (-27)	-0.41 (-26)	-0.42 (-21)	-0.01 (-13)	-0.20 (-23)	-0.43 (-26)	-1.05 (-36)	-1.48 (-32)	-2.30 (-9)	-0.22 (-54)	-0.55 (-24)	-0.49 (-24)	-1.63 (-29)	-2.13 (-28)
NE	OA	-0.84 (-39)	-0.88 (-41)	-0.01 (-1)	0.00 (2)	-0.19 (-29)	-0.88 (-40)	-1.31 (-34)	-2.19 (-36)	9.81 (9)	-0.26 (-44)	-0.54 (-27)	-0.98 (-38)	-1.49 (-24)	-2.48 (-28)
NE	W	-0.48 (-25)	-0.43 (-31)	0.22 (19)	0.02 (29)	-0.06 (-8)	-0.41 (-29)	-0.58 (-20)	-0.99 (-23)	2.95 (13)	-0.11 (-30)	-0.19 (-12)	-0.43 (-26)	-0.64 (-16)	-1.07 (-18)
NE	Sp	-0.90 (-38)	-1.00 (-39)	-0.04 (-6)	0.00 (3)	-0.21 (-30)	-0.99 (-38)	-1.86 (-41)	-2.85 (-40)	-0.03 (0)	-0.33 (-55)	-0.54 (-29)	-1.11 (-36)	-2.28 (-30)	-3.39 (-31)
NE	Su	-1.20 (-48)	-1.54 (-50)	-0.12 (-21)	-0.01 (-23)	-0.29 (-43)	-1.55 (-50)	-1.78 (-36)	-3.33 (-42)	3.21 (11)	-0.39 (-42)	-0.93 (-34)	-1.81 (-47)	-2.06 (-25)	-3.87 (-31)
NE	F	-0.80 (-42)	-0.81 (-47)	-0.09 (-13)	-0.01 (-14)	-0.20 (-34)	-0.81 (-46)	-1.06 (-35)	-1.87 (-39)	2.87 (10)	-0.25 (-50)	-0.50 (-30)	-0.91 (-44)	-1.14 (-23)	-2.05 (-30)
SO	OA	-0.58 (-32)	-0.63 (-35)	-0.01 (-2)	0.00 (-1)	-0.13 (-24)	-0.63 (-34)	-0.70 (-25)	-1.33 (-29)	-3.12 (-2)	-0.22 (-46)	-0.44 (-24)	-0.72 (-32)	-0.85 (-17)	-1.57 (-22)
SO	W	-0.34 (-20)	-0.24 (-21)	0.15 (18)	0.02 (32)	-0.04 (-7)	-0.22 (-19)	-0.43 (-19)	-0.65 (-19)	-3.56 (-11)	-0.17 (-43)	-0.18 (-13)	-0.23 (-16)	-0.57 (-16)	-0.81 (-16)
SO	Sp	-0.59 (-29)	-0.78 (-34)	-0.03 (-6)	0.00 (-3)	-0.14 (-24)	-0.78 (-33)	-0.71 (-21)	-1.49 (-26)	-0.24 (-1)	-0.23 (-50)	-0.43 (-25)	-0.89 (-31)	-0.77 (-12)	-1.66 (-18)
SO	Su	-0.74 (-40)	-0.88 (-41)	-0.09 (-16)	-0.01 (-20)	-0.18 (-35)	-1.00 (-43)	-1.12 (-30)	-2.11 (-35)	0.78 (2)	-0.31 (-46)	-0.69 (-28)	-1.20 (-39)	-1.19 (-19)	-2.41 (-26)
SO	F	-0.66 (-39)	-0.69 (-44)	-0.09 (-16)	-0.01 (-16)	-0.17 (-33)	-0.70 (-43)	-0.56 (-28)	-1.25 (-35)	0.76 (2)	-0.16 (-45)	-0.47 (-28)	-0.80 (-40)	-0.73 (-21)	-1.53 (-28)

Colored entries are significant at p=0.05 level: blue=significant decrease; pink=significant increase.

Figure 4. P1-to-P4 changes expressed in Table 3 units and as relative differences (%); see Table 2 for definitions of column headings.

spheric concentration (e.g., dry SO_4; Fig. 4) and exaggerate increases (e.g., dry NO_3).

In the east and in each geographic region, seasonal P1-to-P4 changes in mean PR are not significant ($p \leq 0.05$; Fig. 4), and they are usually small ($\leq 10\,\%$), except in winter. These wintertime changes contribute to a small, but significant, 1 % increase in PR in the east, 9 % increase in the northeast, and 2 % decrease in the south. Reduced significance of wintertime changes in wet deposition (e.g., wet S, wet OxN, wet H^+, and wet N; Fig. 4) appears to be associated with these numerical wintertime P1-to-P4 changes in PR.

3.2 Oxidized sulfur species

As is illustrated in Fig. 4, significant P1-to-P4 reductions occur in atmospheric SO_2 concentration and dry deposition, atmospheric aerosol SO_4 concentration, atmospheric S concentration and dry deposition, and total S in each region in each season and over all seasons. For atmospheric SO_2 concentration and dry deposition, the numerically largest significant seasonal absolute reductions usually occur in winter when SO_2 concentration is at its seasonal maximum (largest in northeast); the smallest occur in summer when SO_2 concentration is at its seasonal minimum (smallest in south). Both SO_2 concentration and dry deposition show similar P1-to-P4 relative reductions of approximately 50 % across all seasons and regions.

As noted earlier, P1-to-P4 changes in atmospheric aerosol SO_4 concentrations show significant reductions in each region both in each season and over all seasons. Seasonally, the numerically largest absolute and relative reductions tend to occur in summer when aerosol SO_4 concentration is at its seasonal maximum, with regionally uniform summertime absolute reductions of $\approx 3.4\,\mu g\,SO_4\,m^{-3}$ and relative reductions ranging regionally between 38 and 42 %. The regionality of aerosol SO_4 concentration, a secondary pollutant, is also illustrated in Table 3 by contrasting its across-site variability (CV) with that of its precursor, SO_2 (e.g., 22 % vs. 51 %).

Dry deposition of aerosol SO_4 also shows significant P1-to-P4 reductions regionally. Overall relative reductions in

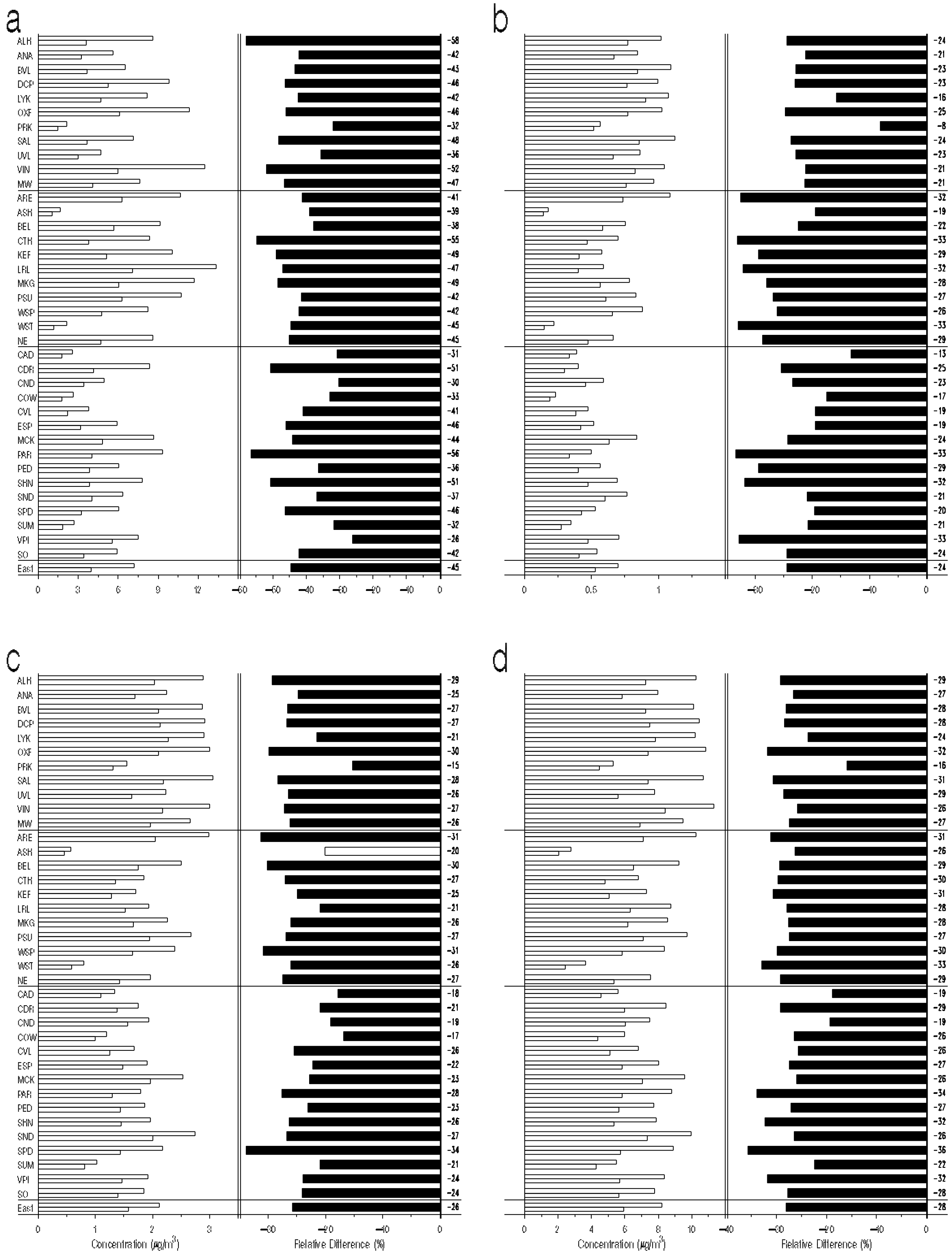


Figure 5. Site- and region-specific concentration ($\mu g\,m^{-3}$, left – upper bar, P1; and lower bar, P4) and P1-to-P4 relative changes (%, right and bottom) for **(a)** S: monitored oxidized sulfur ($\mu g\,S\,m^{-3}$); **(b)** OxN: monitored oxidized nitrogen ($\mu g\,N\,m^{-3}$); **(c)** N: monitored oxidized plus reduced nitrogen ($\mu g\,N\,m^{-3}$); and **(d)** CASTNET PM: sum of aerosol SO_4, NO_3, and NH_4 ($\mu g\,m^{-3}$). Significance level of period-to-period relative changes indicated by bar fill: black, $p \leq 0.05$; and open, $p > 0.05$ (NS). Sites are identified by region in the same order as shown in Table 1.

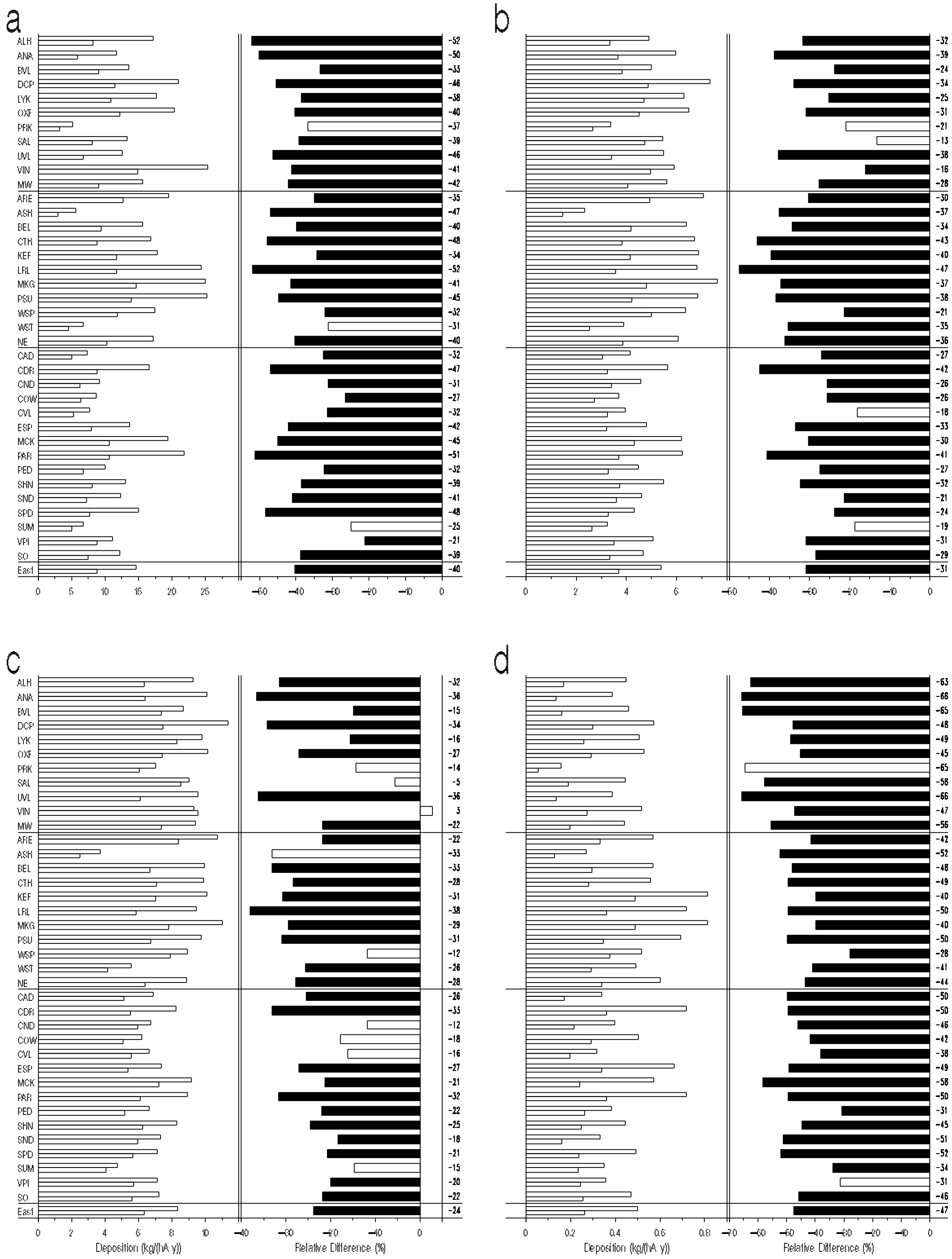


Figure 6. Site- and region-specific total deposition (kg (ha yr)$^{-1}$, left – upper bar, P1; and lower bar, P4) and P1-to-P4 relative changes (%, right and bottom) for **(a)** Total S: total dry plus wet oxidized sulfur deposition; **(b)** Total OxN: sum of dry plus wet deposition of monitored oxidized nitrogen; **(c)** Total N: sum of total dry plus wet deposition of monitored oxidized plus reduced nitrogen; and **(d)** Wet H^+: wet deposition of H^+. Significance level of period-to-period relative changes indicated by bar fill: black, $p \leq 0.05$; and open, $p > 0.05$ (NS). Sites are identified by region in the same order as shown in Table 1.

dry SO_4 are numerically less than the corresponding values for concentration of aerosol SO_4 (i.e., for the east, 29 % vs. 33 %). This pattern is likely due in part to significant period-to-period increases in aerosol Vd, noted earlier. Seasonally, the numerically largest absolute and relative reductions in dry SO_4 tend to occur in summer when aerosol SO_4 concentration is at its seasonal maximum, with an average relative reduction of 37 % in summer in the east. Dry SO_4 shows significant reductions in most seasons, except winter, when its concentration is at a seasonal minimum.

Since atmospheric S concentration is the sum of atmospheric SO_2 and aerosol SO_4 concentrations (expressed as mass of sulfur) and ≈ 67 % of atmospheric S is present as SO_2 (RSO_2; Table 3), the behavior of atmospheric S concentration is dominated by that of SO_2. Additionally, since ≈ 85 % of the dry S is usually contributed by SO_2 ($RFSO_2$; Table 3), the behavior of dry S is likewise dominated by that of dry SO_2. As a result, P1-to-P4 changes of both atmospheric S concentration and dry deposition are similar to those for atmospheric SO_2 concentration and dry deposition, and they are similar to each other (Fig. 4). Atmospheric S concentration and dry S are reduced significantly in each region in each season and over all seasons. Seasonally, the numerically largest significant absolute reductions usually occur in winter when atmospheric SO_2 concentration is at its seasonal maximum, and the largest of these occurs in the northeast. Regionally, P1-to-P4 relative reductions are similar for atmospheric S concentration (42 to 47 %) and dry deposition (48 to 51 %).

In contrast to atmospheric SO_2 concentration (with its summertime minimum), wet S has a seasonal summer maximum. This coincides with scavenging of SO_4 by precipitation when both atmospheric aerosol SO_4 concentration and PR are generally at their seasonal maxima. The numerically largest significant absolute and relative P1-to-P4 reductions in wet S also generally occur in summer. Changes in wet S are numerically smaller and less significant in winter due to seasonal minima of wet S and PR and to wintertime P1-to-P4 increases in PR. In general, relative reductions in wet S are similar to those of aerosol SO_4 concentration (e.g., 33 and 32 % in the east).

Except during winter, wet S generally constitutes more than 50 % of the total S ((D/T) S; Table 3) and exerts a corresponding influence on total S. As noted earlier, P1-to-P4 total S is reduced significantly in each region in each season and over all seasons (Fig. 4). Since seasonal behaviors of dry S and wet S are different but complementary, the seasonal behavior of their sum, total S, shows less seasonal variability than its constituents. Nevertheless, the numerically largest significant P1-to-P4 absolute reductions for total S occur in summer when wet S is at its seasonal maximum. Relative P1-to-P4 reductions are similar across regions, and average 40 % in the east.

3.3 Oxidized nitrogen species

Sampling artifacts described in Sect. 2 suggest that sampling artifacts may provide biases in opposing directions for concentrations of HNO_3 and aerosol NO_3, but these impacts would be minimized during non-summer sampling at non-marine sites. Regional and seasonal changes in atmospheric HNO_3 concentration have more consistent, substantial, and significant reductions for P1-to-P4 (Fig. 4) than for P1-to-P2 or P1-to-P3 (not shown). With recent summertime reductions in NO_x emissions, the seasonal timing of peak HNO_3 concentration has shifted from summer in P1 and P2 to spring in P3 and P4. In addition, P1, P2, and P3 summertime peaks of dry deposition of both HNO_3 and OxN have shifted to spring in P4. The overall P1-to-P4 relative reductions in atmospheric HNO_3 concentration in the east are 34 % vs. 0 % (NS) for P1-to-P2 and 13 % for P1-to-P3. Regionally, the numerically largest significant P1-to-P4 reductions occur in the northeast (39 %), with smaller reductions in the south (32 %) and midwest (30 %). Numerically, maximum absolute and relative seasonal reductions consistently occur in summer, with the largest of these in the northeast. Summertime P1-to-P4 relative reductions in atmospheric HNO_3 concentration are 48 % in northeast, 40 % in south, 38 % in midwest, and 42 % in east. Wintertime P1-to-P4 absolute reductions in atmospheric HNO_3 concentration are smaller, 40 to 46 % of those in summer.

Dry HNO_3 exhibits P1-to-P4 reductions that are of similar magnitude and consistency with those noted above for atmospheric HNO_3 concentration. The only exception is winter in the midwest, where P4 Vd was 9 % higher than in P1. Regionally, significant reductions occur in the northeast (41 %), south (35 %), and midwest (28 %), averaging 35 % in the east. Seasonal behavior of dry HNO_3 is similar to that of atmospheric HNO_3 concentration, with numerically maximum absolute and relative seasonal reductions generally occurring in summer. Summertime P1-to-P4 relative reductions in dry HNO_3 are 50 % in northeast, 41 % in south, 34 % in midwest, and 42 % in east. Wintertime P1-to-P4 absolute reductions in dry HNO_3 are smaller, 20 to 28 % of those in summer.

In contrast to P1-to-P3 comparisons, where atmospheric aerosol NO_3 concentration and dry deposition generally display significant increases (SS07b), P1-to-P4 comparisons in Fig. 4 show more reductions. Significant P1-to-P4 absolute and relative increases in atmospheric aerosol NO_3 concentration and dry NO_3 occur only in winter in the east (e.g., $0.20\,\mu g\,NO_3\,m^{-3}$ and 12 %, and $0.03\,kg\,N\,(ha\,yr)^{-1}$ and 31 %) when atmospheric aerosol NO_3 concentration is at its seasonal maximum. The increased magnitude of winter relative increases in dry NO_3 over those of airborne concentration are likely due to previously noted significant period-to-period increases in aerosols Vd. Wintertime regional absolute P1-to-P4 increases in concentration and dry deposition are numerically strongest in the midwest (e.g., $0.27\,\mu g\,NO_3\,m^{-3}$ and $0.05\,kg\,N\,(ha\,yr)^{-1}$). The wintertime

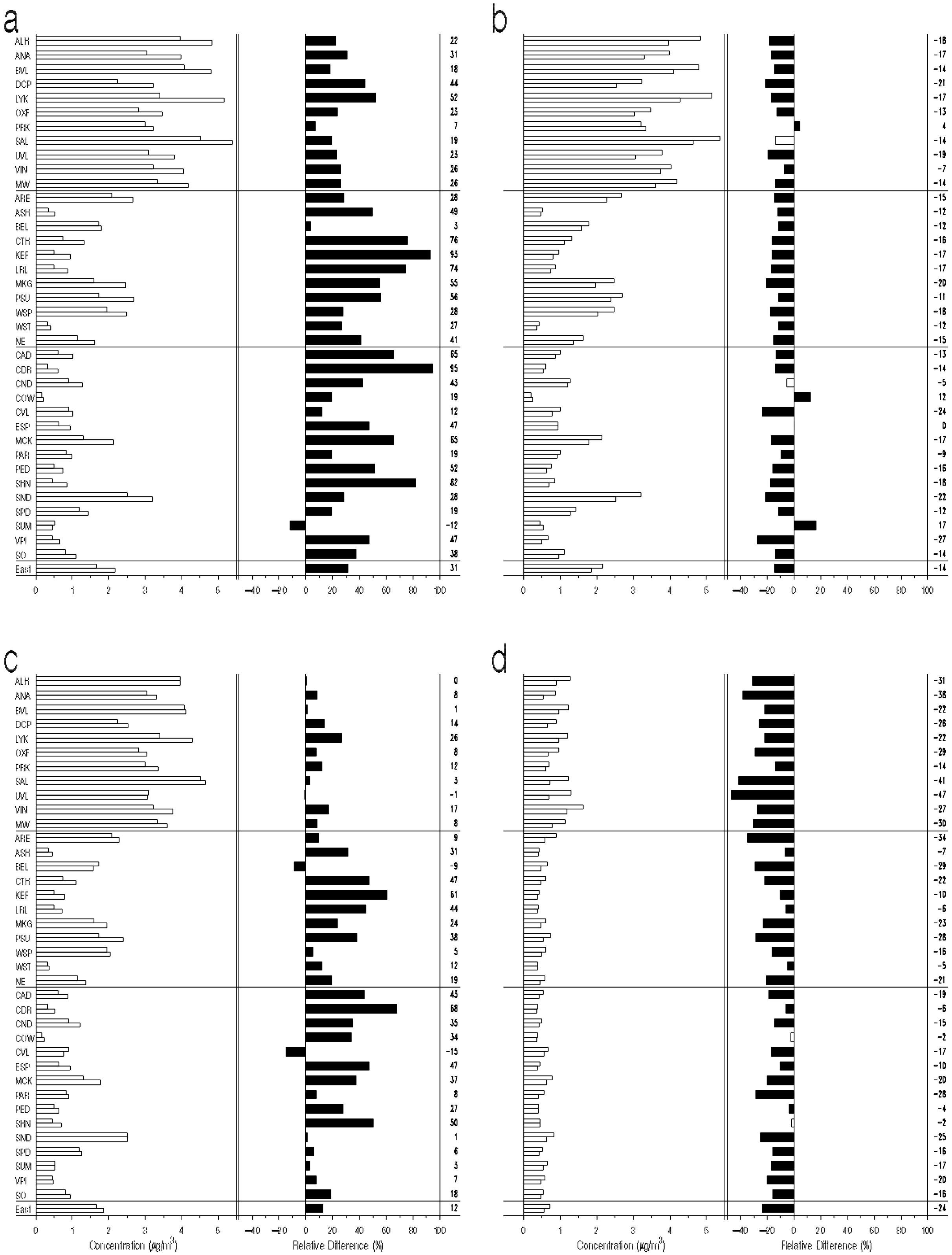


Figure 7. Site- and region-specific seasonal aerosol NO_3 concentration ($\mu g\,m^{-3}$, left – upper bar: early period; and lower bar: later period) and period-to-period relative changes (%, right and bottom) for **(a)** P1-to-P3, W; **(b)** P3-to-P4, W; **(c)** P1-to-P4, W; and **(d)** P1-to-P4, Su. Significance level of period-to-period relative changes indicated by bar fill: black, $p \leq 0.05$; and open, $p > 0.05$ (NS). Sites are identified by region in the same order as shown in Table 1.

P1-to-P4 increases in aerosol NO_3 concentration are considerably smaller than the corresponding P1-to-P3 increases (Fig. 7). Significant P1-to-P4 reductions in absolute and relative atmospheric aerosol NO_3 concentration occur in many of the remaining seasons, especially summer. Significant P3-to-P4 reductions in relative atmospheric aerosol NO_3 concentration occur in all seasons in the east, consistent with recent aggressive reductions of NO_x emissions.

Atmospheric OxN concentration is the sum of atmospheric HNO_3 and aerosol NO_3 concentrations (expressed as mass of nitrogen), and almost 60 % of the OxN is generally present as HNO_3 ($RHNO_{3,}$; Table 3). As a result, the behavior of atmospheric OxN concentration reflects the influence of both atmospheric HNO_3 and aerosol NO_3 concentrations. Also, since well over 90 % of the dry OxN is generally contributed by HNO_3 ($RFHNO_{3,}$; Table 3), the behavior of dry OxN is strongly influenced by that of dry HNO_3. Seasonally in the east, the numerically largest P1-to-P4 absolute and relative reductions in atmospheric OxN concentration and dry deposition (e.g., 0.26 $\mu g\,N\,m^{-3}$ and 38 %, and 1.23 kg N $(ha\ yr)^{-1}$ and 43 %; Fig. 4) occur in summer when atmospheric HNO_3 is the dominant OxN species. Summertime relative reductions are numerically more pronounced in the northeast (43 and 50 %, respectively) than the south (35 and 43 %) or midwest (36 and 34 %). In contrast, in winter, when atmospheric aerosol NO_3 concentration is at its seasonal maximum and significant P1-to-P4 increases of both atmospheric aerosol NO_3 concentration and dry deposition occur, reductions in OxN concentration and dry deposition also occur, but they are smaller in magnitude and in some cases not significant. Over all seasons, regional P1-to-P4 relative reductions in atmospheric OxN concentration and dry deposition are numerically larger in the northeast (29 and 40 %) than the south (24 and 34 %) or the midwest (21 and 27 %), and average 24 and 34 %, respectively, in the east.

Wet OxN and PR in the east are at their seasonal maxima in summer (followed closely by spring). Numerically, the largest significant absolute reductions in wet OxN occur in summer (or spring). Reduced significance of some wintertime P1-to-P4 reductions in wet OxN is associated with numerical increases in wintertime PR. Significant regional P1-to-P4 reductions in wet OxN are numerically larger in the northeast (34 %) than midwest (28 %) or south (25 %), and average 29 % in the east.

Considering the dry deposition of a comprehensive suite of NO_y species, field measurements suggest that 40 to 85 % of total NO_y deposition at eight rural Canadian sites occurred as wet deposition (Zhang et al., 2009), whereas a modeling study suggests that for the continental US this figure is closer to 31 % for NO_y and 44 % for OxN (Zhang et al., 2012). In the current study, over 60 % of the total OxN generally is contributed by wet OxN ((D/T) OxN; Table 3); however, this estimate may be biased because it neglects previously noted uncertainties in Vd for HNO_3 and contributions to dry deposition by non-monitored NO_y species. Nevertheless, wet OxN appears to exert a moderate-to-strong influence on the behavior of total OxN. Both dry OxN and wet OxN display strong seasonal P1-to-P4 reductions in summer that become weaker in winter (Fig. 4). Seasonally, the numerically largest absolute and relative reductions in total OxN occur in summer and range from 42 % in the northeast, to 35 % in the south, to 33 % in the midwest, and average 37 % in the east. Regional P1-to-P4 reductions in total OxN are 36 % in the northeast, 29 % in the south, and 28 % in the midwest, and average 31 % in the east. Thus, over all seasons the numerically largest absolute and relative reductions in atmospheric HNO_3 concentration and dry deposition, atmospheric OxN concentration and dry deposition, and total OxN generally occur in the northeast, and seasonally they tend to occur there in summer.

3.4 Reduced nitrogen species

Since NH_3 is not monitored in CASTNET, aerosol NH_4 is the reduced nitrogen species considered in the current study. Numerically, the regional maximum for atmospheric aerosol NH_4 concentration occurs near emissions sources in the source region and midwest, and the seasonal maximum in the east occurs in summer. As is illustrated in Fig. 4, between P1 and P4, atmospheric aerosol NH_4 concentration shows significant regional relative reductions that are similar, ranging from 29 % in the midwest, to 27 % in the northeast, to 24 % in the south, and averaging 26 % in the east. Seasonally, the numerically largest absolute and relative reductions of atmospheric aerosol NH_4 concentration occur in summer (when atmospheric aerosol SO_4 concentration is at its seasonal maximum and is also experiencing its largest absolute and relative reductions). Summertime P1-to-P4 relative reductions in atmospheric aerosol NH_4 concentration range from 40 % in the midwest, to 32 % in the northeast, to 26 % in the south, and average 32 % in the east. In contrast, reductions are smaller in winter (e.g., 14 % in the east) when atmospheric aerosol NH_4 concentration is small and atmospheric aerosol SO_4 concentration is also at its seasonal minimum.

Although generally showing significant reductions, dry deposition of atmospheric aerosol NH_4 shows numerically weaker P1-to-P4 changes than its atmospheric concentration. The overall P1-to-P4 relative reduction for dry NH_4 in the east (22 %) is numerically smaller than the corresponding value for its atmospheric concentration. This pattern of weaker reductions is likely due to the significant P1-to-P4 increases in aerosol Vd, noted earlier. Regional P1-to-P4 relative reductions in dry NH_4 are 26 % in the northeast and 21 % in the midwest and south. Seasonally, in winter, when the atmospheric aerosol NH_4 concentration is low, changes in its dry deposition show changes which tend to be small and not significant regionally. Mirroring aerosol NH_4 concentration, the numerically largest P1-to-P4 absolute and relative reductions in dry NH_4 also occur in summer. They range from 34 % in the northeast, to 33 % in the midwest, to 24 % in the south, and average 30 % in the east.

Numerically, wet NH_4 is also high near emissions sources in the midwest and source region, and in the east in the spring and summer seasons when PR is also relatively high. At the regional and seasonal scales, wet NH_4 shows P1-to-P4 changes that are usually not significant. The only two reductions that are significant occur overall in the midwest (12 %) and east (9 %). Two wintertime increases occur in the midwest and the east, but they are not significant.

Since the magnitude of wet NH_4 is over seven times larger than dry deposition ((D/T) NH_4; Table 3), the behavior of total NH_4 is strongly influenced by the behavior of wet NH_4. Similar to wet NH_4, total NH_4 shows mostly P1-to-P4 reductions that are usually not significant, but with non-significant wintertime increases in the midwest and the east. The only significant reduction is overall in the east (11 %).

3.5 Oxidized plus reduced nitrogen species

The sum of monitored oxidized and reduced nitrogen species is represented as N. The behavior of the resulting N metrics (i.e., atmospheric N concentration, dry N, wet N, and total N) reflects the behavior of the weighted sum of the individual constituents, described previously.

Aerosol NH_4 constitutes ≈ 67 %, $HNO_3 \approx 19$ %, and aerosol $NO_3 \approx 14$ % of the monitored airborne N concentration (RNNH4 and RNHNO3; Table 3). As a result, aerosol NH_4 exerts a moderate-to-strong influence on its behavior. Seasonally, the numerically strongest absolute and relative P1-to-P4 reductions of atmospheric N concentration occur in summer (midwest, 39 %; northeast, 34 %; south, 28 %; and east, 33 %). This seasonality coincides with the summer peaks of atmospheric N concentration and P1-to-P4 reductions in the concentration of aerosol NH_4, HNO_3, and OxN. Regionally, atmospheric N concentration shows relative reductions of 26 % in the midwest, 27 % in the northeast, 24 % in the south, and 26 % in the east.

Due to the large difference in deposition velocities, ≈ 75 % of dry N is contributed by dry HNO_3, but only ≈ 21 % by dry NH_4 and ≈ 4 % by dry NO_3 (RNFHNO3 and RNFNH4; Table 3). Seasonally, the numerically strongest absolute and relative P1-to-P4 reductions in dry N mirror those of aerosol NH_4, HNO_3, and OxN concentration and dry deposition (and N concentration); they occur in summer (northeast, 47 %; south, 39 %; midwest, 34 %; and east, 40 %). Regional non-significant wintertime P1-to-P4 reductions may result in part from corresponding significant regional increases in dry NO_3. Regionally, the numerically largest P1-to-P4 reductions occur in the northeast (38 %), with smaller reductions in the south (32 %) and midwest (26 %), and they average 32 % in the east.

Wet OxN and wet NH_4 contribute similarly to wet N, with maxima in spring or summer (Table 3). The numerically largest significant P1-to-P4 absolute reductions in wet N also occur in spring or summer, and peak seasonal relative reductions range between 20 and 30 %. Non-significant numerical wintertime P1-to-P4 reductions in wet N occur in the northeast and south, with a non-significant increase in the midwest. This behavior is likely associated with previously noted numerical wintertime P1-to-P4 increases in PR. Regional P1-to-P4 relative reductions in wet N are 24 % in the northeast, 20 % in the midwest, 17 % in the south, and average 20 % in the east.

Since wet N contributes ≈ 75 % of total N ((D/T) N; Table 3), the behavior of total N is strongly influenced by the behavior of wet N. The numerically largest significant P1-to-P4 absolute reductions in total N generally occur in summer, with corresponding seasonal relative reductions of 31 % in northeast, 25 % in midwest, and 26 % in south. Non-significant P1-to-P4 reductions in total N occur only in wintertime and are associated with similar behavior of wet OxN and wet N and numerical wintertime P1-to-P4 increases in PR. Regionally, the numerically largest P1-to-P4 reductions occur in the northeast (28 %), with smaller reductions in the midwest and south (22 %). The overall P1-to-P4 relative reduction of total N in the east is 24 %.

3.6 Wet H^+

Regionally, wet H^+ deposition is generally heaviest in the northeast, and seasonally in the east it is heaviest during summer (Table 3). Seasonally, the numerically largest absolute reductions occur in summer, with relative reductions of similar magnitude in spring and summer, while generally smaller reductions occur in winter (Fig. 4). The numerically largest seasonal relative reductions range from 65 % in the midwest (summer), to 55 % in the northeast (spring), to 50 % in the south (spring). Regionally, P1-to-P4 regional relative reductions of wet H^+ are numerically larger near sources in the midwest (56 %) and smaller in the south (46 %) and northeast (44 %). The overall P1-to-P4 relative reduction in wet H^+ in the east is 47 %.

3.7 Atmospheric O_3 concentration and dry deposition

In the current study, hourly atmospheric O_3 concentrations, averaged to weekly values, are treated as other weekly CASTNET data (i.e., averaged to period–site–season means); however, this does not represent the relevant time period for determining compliance with the US ambient air quality standard. As is illustrated in Fig. 4, mostly non-significant P1-to-P4 seasonal increases in atmospheric O_3 concentration occur in winter in the northeast (13 %, NS), midwest and south (7 %, NS), and east (9 %, significant). Summertime atmospheric O_3 concentrations do show substantial and mostly significant absolute and relative reductions in each region: 6.7 ppb (17 %) in the northeast, 5.3 ppb (14 %) in the south, 2.4 ppb (6 %, NS) in the midwest, and 4.9 ppb (12 %) in the east. The numerically largest reduction in atmospheric O_3 concentration occurs in summer and in the northeast, coinciding with aggressive O_3-season NO_x emissions controls during P3 and P4 in this region and upwind in the east. Unpublished examination of seasonal NO_x emissions in the eastern US for the period between 1990–1992 and 2006–2008 (roughly corresponding to P1-to-P4) suggests that reductions in summertime emissions are approximately 6 % greater than those for the aggregate of the remaining three seasons over the same time period. Regional reductions of atmospheric O_3 concentration over all seasons are small and only significant in the south (5 %) and east (4 %).

Moderate P1-to-P4 increases in Vd for O_3 act in opposition to corresponding reductions in atmospheric O_3 concentration to yield P1-to-P4 changes in dry deposition of O_3 that are sometimes significant. Relatively large, significant seasonal reductions in dry O_3, ranging from 5 to 15 %, occur regionally in summer; however, corresponding increases ranging between 15 and 25 % occur in winter. Regionally, P1-to-P4 reductions in dry O_3 occur in the northeast (8 %) and south (4 %), and a non-significant increase occurs in the midwest (1 %, NS). The P1-to-P4 relative reduction in dry O_3 in the east is 4 %.

4 Discussion

4.1 Changes in atmospheric aerosol SO_4 and SO_2 concentration

Both P1-to-P4 absolute and relative changes in atmospheric aerosol SO_4 concentration, shown in Fig. 4, are numerically substantially less than the corresponding values for atmospheric SO_2 concentration, consistent with the findings of Reid et al. (2001), Holland et al. (2004), and SS07b for earlier time periods. For regional groupings of sites and in the east, the year-round ratios of P1-to-P4 relative reductions in atmospheric aerosol SO_4 concentration to atmospheric SO_2 concentration are similar (≈ 0.7 % decrease in aerosol SO_4 for each 1 % decrease in SO_2). In the east these ratios range numerically between a wintertime low (≈ 0.5 % SO_4 per 1 % SO_2) and a high (≈ 0.8 % SO_4 per 1 % SO_2) in summer when aerosol SO_4 levels are at their seasonal maxima and SO_2 levels are at their seasonal minima. Year-round ratios of P1-to-P4 absolute reductions of atmospheric aerosol SO_4 concentration to those of SO_2 concentration (both expressed as mass of sulfur) are similar in regions of higher emissions density, the midwest and northeast ($\approx 0.2\,\mu g\,S\,m^{-3}$ decrease in aerosol SO_4 for each $1\,\mu g\,S\,m^{-3}$ decrease in SO_2). This ratio is numerically higher in the south (≈ 0.3), and it may be due in part to concurrent reductions of SO_2 emissions in areas of higher emissions density with subsequent transport of reduced amounts of oxidized sulfur, especially aerosol SO_4, into the south.

RSO_2 (Table 3) is the ratio of atmospheric SO_2 concentration to total atmospheric S concentration, and 1-RSO_2 is the relative amount of atmospheric S concentration present as aerosol SO_4, representing a rough index of the extent of conversion of SO_2 to other oxidized sulfur species (i.e., aerosol SO_4). Significant P1-to-P4 RSO_2 reductions (not shown) of 8 % in the south, 5 % in the northeast, and 7 % in the midwest and east correspond to increases in the conversion index (e.g., 17 % in the east). This suggests that as the P1-to-P4 atmospheric SO_2 concentration in the east has decreased, the relative amount of airborne S present as SO_2 has decreased, and both the relative amount present as aerosol SO_4 and the apparent extent of conversion of SO_2 to aerosol SO_4 have increased.

4.2 Changes in dry and wet deposition

As noted in Sect. 3.2, wet S exceeds dry S in the east, except in winter. The P4 ratio of dry S to total S in the east is 0.37 ((D/T) S; Table 3), down from 0.44 in P1; further, qualitatively similar behavior is noted for the BKG sites (i.e., P4 ratio 0.23 vs. 0.26 in P1) and HE sites (i.e., P4 ratio 0.40 vs. 0.50 in P1). In the east, the ratio of dry S to wet S (calculated from (D/T) S) has diminished by 24 % from P1 (0.78) to P4 (0.60). This reduction is strongest (> 30 %) in regions of high emissions density (midwest and northeast) in winter, where SO_2 concentrations are at their peak. Year-round, in the east and regionally, both P1-to-P4 absolute and relative reductions in dry S are numerically larger (by ≈ 20 to 70 %; Fig. 4) than corresponding values for wet S. However, in summer when PR is high and atmospheric aerosol SO_4 concentration is at its seasonal maximum, the absolute P1-to-P4 reductions are larger (by ≈ 25 to 100 %) for wet S than dry S. In other seasons, the roles are different, and in winter, when atmospheric SO_2 concentration is at its seasonal maximum and PR is at its seasonal minimum, P1-to-P4 absolute and relative reductions in dry S are substantially larger (by over a factor of ≈ 2) than the corresponding reductions for wet S. Thus, strong emissions controls of the primary pollutant SO_2 have reduced dry S to a greater extent than wet S, permitting the latter to become an increasing relative contributor to total S. This, along with the increased apparent conversion of SO_2 to aerosol SO_4, noted above, suggests that wet processes are becoming more prominent than dry processes at removing oxidized sulfur from the current atmosphere in the east.

Whereas deposition estimates of both primary and secondary oxidized sulfur species are available for comparison of their dry and wet P1-to-P4 changes, only changes in deposition of monitored secondary oxidized nitrogen species can be compared in the current study. In the east, dry OxN appears to be numerically smaller than wet OxN (Sect. 3.3), and the P4 ratio of dry OxN to total OxN is 0.35 ((D/T) OxN; Table 3), down slightly from 0.37 in P1. Qualitatively similar behavior is noted for the BKG sites (i.e., P4 ratio 0.27

vs. 0.30 in P1) and HE sites (i.e., P4 ratio 0.41 vs. 0.51 in P1). Absolute P1-to-P4 reductions in dry OxN are generally numerically smaller than corresponding values for wet OxN (Fig. 4). However, with the recent, more aggressive NO_x emissions controls, the relative P1-to-P4 reductions of dry OxN now exceed those for wet OxN more frequently than in the earlier P1-to-P3 comparison (SS07b). These findings suggest that wet OxN is becoming an increasing relative contributor to total OxN.

4.3 CASTNET PM

Although $PM_{2.5}$ is not monitored in CASTNET, many of the major inorganic constituents (i.e., aerosol SO_4, NO_3, and NH_4) are monitored. In contrast to aerosol SO_4 and NH_4, which occur mainly as fine particles, there is evidence suggesting that aerosol NO_3 can be multi-modal in the east and is subject to sampling artifacts in opposing directions with the CASTNET sampler, but they are thought to be minimal during cooler seasons at the non-marine, eastern CASTNET sites (see Sect. 2). In the current study, CASTNET PM is taken to be the sum of atmospheric aerosol SO_4, NO_3, and NH_4 mass concentrations.

Significant P1-to-P4 (Fig. 5) and P3-to-P4 reductions occur in CASTNET PM concentration in each region in each season and over all seasons. This is in contrast to P1-to-P3 behavior where non-significant wintertime changes occurred (SS07b), with both numerical and significant increases in the midwest (Fig. 8). Year-round absolute and relative reductions in the east are $2.3\,\mu g\,m^{-3}$ and 28 % (P1-to-P4) and $1.1\,\mu g\,m^{-3}$ and 16 % (P3-to-P4). Seasonally, they peak in summer when aerosol SO_4 and NH_4 concentrations are at their maxima and are also experiencing their largest reductions. Regionally, the largest absolute and relative reductions in CASTNET PM occur in the midwest in summer ($4.9\,\mu g\,m^{-3}$ and 41 % – P1-to-P4 and $1.9\,\mu g\,m^{-3}$ and 21 % – P3-to-P4).

For the chemically complex NH_3–HNO_3–H_2SO_4 water system, conditions can arise where the availability of NH_3 limits the formation of aerosol NH_4NO_3. Here, subsequent reductions of airborne aerosol SO_4, by tying up less NH_3 as aerosol $(NH_4)_2SO_4$, may make more NH_3 available to react with HNO_3, increasing the level of aerosol NH_4NO_3. Although atmospheric NH_3 concentration is not monitored in CASTNET, when the index, RNO_3 (i.e., the ratio of atmospheric aerosol NO_3 to OxN concentrations), is less than 0.7, then formation of aerosol NH_4NO_3 may be NH_3-limited (Blanchard et al., 2000). Using this index and focusing on non-summer season results to minimize the impacts of sampling artifacts (see Sect. 2), results in Table 3 suggest that NH_3-limited conditions are present in the east but are weakest in winter and year-round in the midwest.

Significant P1-to-P2-to-P3-to-P4 increases in RNO_3 occur in the east. Regionally, the numerically largest absolute and relative P1-to-P4 increases occur in the northeast (40 %), with smaller increases in the south (28 %), midwest (10 %), and east (22 %). Seasonally, the numerically largest absolute increases occur in winter. The numerically largest regional P1 winter RNO_3 value (0.70) occurs in the midwest, and this value increases significantly by 12 % to 0.78 in P4. These results suggest that between P1 and P4, NH_3 availability has increased in the east and the formation of aerosol NO_3 has become less NH_3-limited. The least NH_3-limited situation appears to occur in winter in the midwest (with its strong sources of NH_3). In addition, the relative amount of monitored OxN present as HNO_3, $RHNO_3$ (i.e., 1-RNO_3), diminished significantly in the east between P1 (0.66) and P4 (0.59) (Sect. 3.3).

For a chemical system initially containing NH_3, HNO_3, H_2SO_4, and water, an index of the extent to which ambient sulfuric acid (H_2SO_4) has been neutralized by atmospheric NH_3 may be defined as the neutralization index (NI). Correcting for the presence aerosol NH_4NO_3, it may be computed as $([NH_4] - [NO_3])/2[SO_4]$ (Blanchard and Hidy, 2005). The value of NI can range between zero (un-neutralized H_2SO_4) and unity (100 % neutralization to $(NH_4)_2SO_4$). As shown in Table 3, NI averages ≈ 0.8 in the east. Calculation of NI assumes that aerosol NO_3 is present as fine aerosol NH_4NO_3 and neglects the possible presence other forms of aerosol NO_3 (e.g., from large particle sea/road salt or soil/mineral dust). As suggested in Sect. 2, sampling artifacts may provide biases in opposing directions for aerosol NO_3. Their impacts are expected to be minimal during cooler season sampling at non-marine sites. Although small (but significant) P1-to-P4 increases in NI occur in the east, large increases occur in summer in the northeast (15 %) and south (18 %), while small non-significant decreases occur in winter. These results suggest that between P1 and P4 an acidic aerosol is approaching neutralization due to increased relative availability of NH_3 associated with reductions of aerosol SO_4 concentration. These findings are consistent with those noted in previous paragraphs and with those for P1-to-P3 (SS07b), indicating that conditions in the east are becoming less NH_3-limited.

Modeling efforts have indicated that nonlinear changes in $PM_{2.5}$ concentrations can occur in response to reductions in atmospheric aerosol SO_4 concentrations in the east (Ansari and Pandis, 1998; West et al., 1999; Blanchard and Hidy, 2005). Under NH_3-limited conditions Blanchard et al. (2000) suggest that reduction of aerosol SO_4 concentrations can increase aerosol NO_3 concentrations by amounts that exceed the aerosol SO_4 reductions on a mass basis, and that reductions of ambient oxidized nitrogen concentrations (that may accompany reductions in NO_x emissions) may not reduce aerosol NO_3 concentrations. These modeling studies suggest that for the NH_3–HNO_3–H_2SO_4 water system, constituent concentration and temperature conditions can exist in the east so that when the atmospheric aerosol SO_4 concentration is reduced, the corresponding change in $PM_{2.5}$ concentration can be influenced nonlinearly. At low temperatures, aerosol

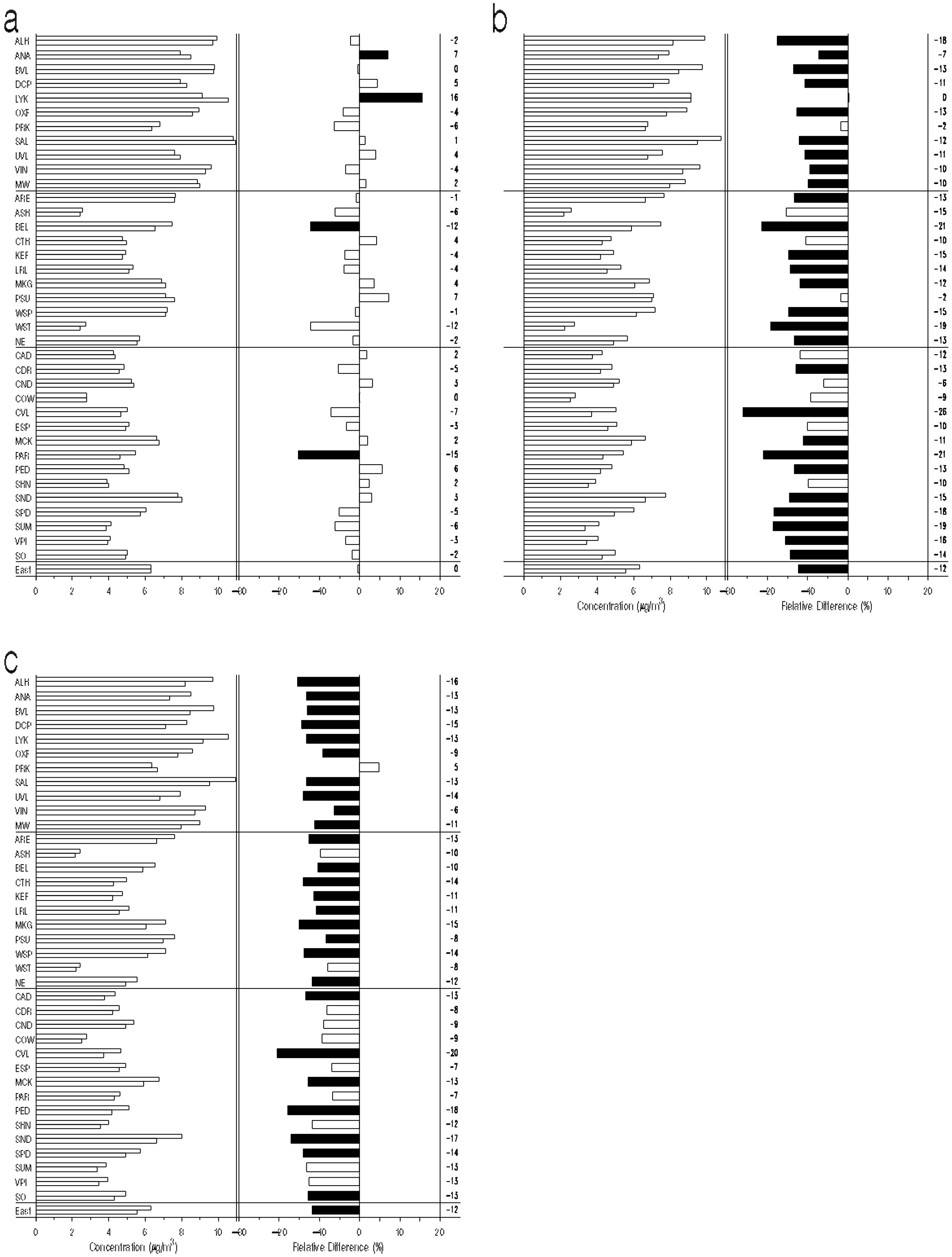


Figure 8. Site- and region-specific wintertime CASTNET PM concentration (µg m^{-3}, left – upper bar: early period; and lower bar: later period) and period-to-period relative changes (%, right and bottom) for **(a)** P1-to-P3, W; **(b)** P1-to-P4, W; and **(c)** P3-to-P4, W. Significance level of period-to-period relative changes indicated by bar fill: black, $p \leq 0.05$; and open, $p > 0.05$ (NS). Sites are identified by region in the same order as shown in Table 1.

NH_4NO_3 will likely form when NH_3 is made available from a reduction in atmospheric aerosol SO_4 concentration, and negative to nonlinear responses ranging from -0.3 to < 1.0 (Δµg $PM_{2.5}/\Delta$µg SO_4) can result (Ansari and Pandis, 1998; West et al., 1999). Using model estimates, West et al. (1999) have predicted that these conditions would exist most commonly in winter in the midwest and would be uncommon in summer in the east. A 2009 field study (Stanier et al., 2012) has focused on wintertime episodes of elevated aerosol NO_3 concentrations in the midwest (Wisconsin).

Ratios of P1-to-P4 absolute changes in CASTNET PM concentrations to corresponding changes in aerosol SO_4 – Δ(µgCASTNET PM m^{-3})/Δ(µg SO_4 m^{-3}) – have been determined. Year round, these ratios are of similar magnitude, numerically falling between 1.2 and 1.6, both for the east and for each regional grouping of sites. Seasonally in the east, these ratios range between 1.3 and 1.5 in spring, summer, and fall. However, in winter they are numerically close to 1.0 in the east and each region. This represents a change from P1-to-P3 behavior, where the wintertime ratio averaged close to 0.0 in the east, and in the midwest was negative and accompanied by a numerical increase in CASTNET PM (SS07b). Wintertime numerical increases in CASTNET PM occurred at 15 sites between P1 and P3, but at only one site between P1 and P4 and at only one site between P3 and P4 (Fig. 8). This wintertime behavior of CASTNET PM appears to be driven largely by that of aerosol NO_3 (Fig. 7). These findings suggest that additional P3-to-P4 reductions in emissions of SO_2, and especially NO_x, have made progress in altering the chemical regime of the wintertime eastern US atmosphere so that future emissions reductions and their resulting reductions in aerosol concentrations may no longer be accompanied by sub-linear changes (or actual increases) in CASTNET PM.

4.4 Comparison with emissions estimates

Emissions estimates for SO_2 and NO_x (Xing et al., 2013) have been aggregated to regional levels and have been used to determine current mean estimates of P1, P2, P3 and P4 emissions as well as period-to-period absolute and relative changes in regional SO_2 and NO_x emissions in the east (see Sect. 2.1 for identification of the states composing each geographical region). Although current P1, P2, and P3 emissions estimates have been updated and may be slightly different compared to those reported in SS07b, using the same current version permits period-to-period comparisons to be made using consistent emissions estimates. In addition, subsequent analyses, repeated using emissions estimates (US EPA, National Emissions Inventory, Emissions Factor and Inventory Group, Office of Air Quality Planning and Standards, Research Triangle Park, NC, http://www.epa.gov/ttn/chief/net/2008inventory.html, accessed 02/12/13), yielded reasonably consistent findings with no appreciable changes to conclusions.

Continuous emissions monitors used on most EGUs provide reasonably accurate estimates of SO_2 and NO_x emissions from these sources. Although EGUs are the main source of SO_2 emissions; EGUs, on-road, and off-road sources contribute substantially to total NO_x emissions. Uncertainty in on-road and other non-EGU NO_x emissions make estimates of total NO_x emissions more uncertain than those for SO_2 (Butler et al., 2005; Parrish, 2006; Blanchard et al., 2013).

Estimates of both P1 and P4 emissions density are shown in Table 4 in the same units as deposition. For example, the P1 emissions density for SO_2 is over 60 % higher in the midwest, with its EGU sources in the Ohio Valley, than in the south (i.e., 51 vs. 31 kg S (ha yr)$^{-1}$). P1-to-P4 relative change results for regional SO_2 and NO_x emissions (Fig. 3) are also shown in Table 4 with corresponding values for selected measures of atmospheric concentration and total deposition from Fig. 4.

4.4.1 Oxidized sulfur species

The fairly universal reductions in the S-related concentration and deposition metrics noted previously in Sect. 3.2 largely reflect the year-round SO_2 emissions controls that have been continuing since 1995 (Fig. 1). Reductions in SO_2 emissions in the east have led to significant reductions in monitored SO_2 concentrations, i.e., P1-to-P2 (21 vs. 27 %), P1-to-P3 (35 vs. 33 %), P1-to-P4 (50 vs. 48 %), and P3-to-P4 (23 vs. 23 %). Reductions in SO_2 emissions in the east have led to significant, but smaller, reductions in aerosol SO_4 concentrations, i.e., P1-to-P2 (21 vs. 12 %), P1-to-P3 (35 vs. 21 %), P1-to-P4 (50 vs. 33 %), and P3-to-P4 (23 vs. 15 %).

As indicated in Table 4, the P1-to-P4 relative reductions in SO_2 emissions in the east (50 %) are in closer numerical agreement with reductions of atmospheric concentration of the monitored primary pollutant, SO_2 (48 %), than the monitored reaction product, aerosol SO_4 (33 %). Ratios of the P1-to-P4 relative change in monitored concentration to emissions estimates for SO_2 in the east are approximately 0.97 for SO_2 and 0.66 for aerosol SO_4, with similar findings for P3-to-P4 comparisons. Relative P1-to-P4 comparisons also show significant reductions for SO_2 emissions (50 %) and dry S (49 %). These results suggest that at the current scale, the responses of both atmospheric SO_2 concentration and dry deposition to changes in SO_2 emissions are close to 1 : 1; however, the relationship appears to be less than 1 : 1 for aerosol SO_4. In addition, as indicated here and in Sect. 4.1, the relationship between changes in the concentration of the reaction product, aerosol SO_4, and that of the primary pollutant, SO_2, appears to be less than 1 : 1.

These findings are generally consistent with earlier findings for P1-to-P3 comparisons (SS07b) as well as those of those of others. Butler et al. (2001) reported slightly less than a 1 : 1 relationship between changes in downwind atmospheric S concentration and changes in SO_2 emissions

Table 4. P1 and P4 emissions density and P1-to-P4 relative changes (%) in oxidized sulfur and nitrogen emissions, atmospheric concentration, and dry, wet, and total deposition.

	Emissions		P1-to-P4 Change in atmospheric concentration			P1-to-P4 Change in deposition			
Region	ρ_1^a (ρ_4)	P1-to-P4 Change	SO_2	SO_4	S	Dry S	Wet S	Total S	Wet H^+
E	38 (19)	−50	−48	−33	−45	−49	−32	−40	−47
MW	51 (23)	−55	−51	−33	−47	−48	−36	−42	−56
NE	36 (19)	−47	−48	−34	−45	−51	−30	−40	−44
SO	31 (16)	−47	−47	−32	−42	−49	−31	−39	−46
	ρ_1^b (ρ_4)	P1-to-P4 Change	HNO_3	NO_3	OxN as N	Dry OxN	Wet OxN	Total OxN	Wet H^+
E	19 (11)	−42	−34	−8	−24	−34	−29	−31	−47
MW	21 (12)	−43	−30	−13	−21	−27	−28	−28	−56
NE	23 (12)	−46	−39	-1^c	−29	−40	−34	−36	−44
SO	17 (10)	−39	−32	-2^c	−24	−34	−25	−29	−46

[a] SO_2 emissions density in units of kg S (ha yr)$^{-1}$.
[b] NO_x emissions density in units of kg N (ha yr)$^{-1}$.
[c] $p > 0.05$, NS.

from specific upwind source regions. Blanchard et al. (2013) found southeastern US trends of SO_2 ambient concentrations and emissions to be decreasing with a qualitative 1 : 1 proportionality, while the relationship for trends of ambient aerosol SO_4 concentrations and SO_2 emissions were decreasing but at less than 1 : 1 proportionality. Hand et al. (2012) reported linear relationships between aerosol SO_4 concentrations and SO_2 emissions that depended on location in the US, with aerosol SO_4 concentration showing the weakest response to SO_2 emissions in a region in the eastern US roughly included in the currently defined source region, midwest, and northeast.

Atmospheric pollutants are transported and transformed by physical and chemical processes between their release and deposition. For example, gaseous SO_2 may be transformed into aerosol SO_4 by several pathways, including gas-phase oxidation by the hydroxyl radical and, after dissolution in water droplets, via oxidation by hydrogen peroxide and O_3 (McHenry and Dennis, 1994). As SO_4-containing aqueous particles undergo atmospheric processing (i.e., evaporation and dissolution), there is a close linkage between the secondary pollutant's atmospheric concentration and wet removal (i.e., they have similar atmospheric timescales). Although SO_4 is then subject to both dry and wet deposition, the latter dominates (e.g., east P4 wet S is 5.2 kg S (ha yr)$^{-1}$ vs. 0.4 kg S (ha yr)$^{-1}$ for dry SO_4; Table 3). This may explain the relatively good agreement between P1-to-P4 (33 %) and P3-to-P4 (15 %) reductions in the atmospheric concentration of secondary pollutant, aerosol SO_4, and corresponding changes (32 and 13 %) in wet S.

Since atmospheric S concentration is comprised of SO_2 and aerosol SO_4, reductions of SO_2 emissions may be expected to yield responses of atmospheric S concentration and total S that fall between corresponding values for SO_2 and aerosol SO_4. This is confirmed in Table 4 where reductions in SO_2 emissions in the east correspond to significant reductions of both atmospheric S concentration (i.e., P1-to-P4, 50 vs. 45 %) and total S (i.e., P1-to-P4, 50 vs. 40 %).

For a pollutant where all primary and secondary species are monitored (e.g., S), neglecting other sources and sinks, emissions density may be compared with total deposition to construct rough budgets for oxidized sulfur, revealing insights about the relative amounts of the species deposited and exported. Model predictions for North America (Wojcik and Chang, 1997) suggest approximately 50 % of S emissions are deposited. In the current study, P1, P2, P3 and P4 S emissions densities in the east are 38, 30, 25, and 19 kg S (ha yr)$^{-1}$, while corresponding total S values are 15, 12, 11 and 8.7 kg S (ha yr)$^{-1}$. Between P1 and P4 the relative amount of deposited S emissions increased by $\approx$ 8 % from 39 to 47 %, and the net exported S emissions decreased by a corresponding amount from 61 % to 53 %. Thus, the strong P1-to-P4 SO_2 emissions controls are accompanied by increased apparent conversion of SO_2 to aerosol SO_4 (Sect. 4.1), possible increased relative contribution of wet vs. dry deposition (Sect. 4.2), increased fraction of deposited S emissions, and decreased fraction of exported S emissions.

4.4.2 Oxidized nitrogen species

Changes in pollutant emissions generally lead to more direct changes in the atmospheric concentration of primary rather than secondary pollutant species, where emissions as well as variable meteorological and atmospheric chemical processes are influential. In contrast to oxidized sulfur species, where the behaviors of both primary and secondary pollutants are monitored, the atmospheric concentration and deposition of only a few of the secondary oxidized nitrogen species (i.e., HNO_3, aerosol NO_3 and aqueous NO_3 ion) are monitored in the current study. This likely propagates more uncertainty into comparisons with primary NO_x emissions than is present in earlier comparisons with SO_2 emissions.

Recent aggressive NO_x emissions controls in the east have led to significant reductions in concentrations of the important secondary oxidized nitrogen pollutant, HNO_3, i.e., P1-to-P2 (6 % vs. NS), P1-to-P3 (22 vs. 13 %), P1-to-P4 (42 vs. 34 %), and P3-to-P4 (25 vs. 24 %). The nonlinear behavior of aerosol NO_3 concentration noted in Sect. 4.3 is apparent in many comparisons of reductions in NO_x emissions with aerosol NO_3 behavior but appears to be diminishing with time (i.e., P1-to-P2 (6 vs. −5 %), P1-to-P3 (22 vs. −11 %), P1-to-P4 (42 vs. 8 %), and P3-to-P4 (25 vs. 17 %), where the minus sign indicates increase).

The numerically largest P1-to-P4 relative reductions in estimated NO_x emissions (46 %), year-round atmospheric concentrations of HNO_3 (39 %) and OxN (29 %), dry OxN (40 %), wet OxN (34 %), total OxN (36 %), and summertime total OxN (42 %) occur in the northeast, the region with the largest P1 emissions density (Table 4). As noted in Sect. 3.3, numerical maximum absolute and relative seasonal reductions in atmospheric HNO_3 concentrations also occur in summer, with largest reductions in the northeast. These changes are likely reflecting contributions from year-round control of NO_x emissions by Phases I and II of the CAAA and continuing mobile source controls. However, the timing (e.g., changes most apparent in summer with peak concentrations moving from summer to spring) and the location (i.e., strongest reductions in northeast) suggest that major contributors are summertime NO_x emissions control activities instituted under OTC, SIP Call, BTP and CAIR that focused on EGU sources in the eastern states.

As noted above and in SS07b, the 22 % reduction in the east of P1-to-P3 NO_x emissions is associated with a 13 % reduction in HNO_3 concentration, an 8 % reduction in dry OxN, a 12 % reduction in wet OxN, an 11 % reduction in total OxN, but an 11 % increase in aerosol NO_3 concentration. Here, the ratio of P1-to-P3 relative changes of monitored HNO_3 concentration to those of estimated NO_x emissions is 0.6, qualitatively consistent with the value of 0.7 found by Butler et al. (2005) for a similar time period (1991–2001). Recent aggressive NO_x emissions controls, however, appear to have altered these relationships. As indicated in Table 4, the 42 % P1-to-P4 reduction of NO_x emissions in the east corresponds to 34 % reductions in HNO_3 concentration and dry OxN, a 29 % reduction in wet OxN, a 31 % reduction in total OxN, and an 8 % reduction in aerosol NO_3 concentration. Here, the ratio of P1-to-P4 relative changes of monitored HNO_3 concentration and dry OxN to those of estimated NO_x emissions is 0.8, but the corresponding ratio for aerosol NO_3 concentration is 0.2. These findings are consistent with the recent observations in the southeastern US of decreasing 1999–2010 trends of NO_y concentration that exceed those for aerosol NO_3 concentration and are qualitatively proportional to decreasing NO_x emissions trends (Blanchard et al., 2013).

In the east, the 42 % P1-to- P4 reduction of NO_x emissions also corresponds to significant reductions of deposition, i.e., dry HNO_3 (35 %), dry OxN (34 %), wet OxN (29 %) and total OxN (31 %). The relatively good agreement between the P1-to-P4 changes in the atmospheric concentration of HNO_3, dry HNO_3, and dry OxN can be explained by the high $RFHNO_3$ (Sect. 3.3; Table 3). The favorable comparison with wet OxN may be related to the high relative abundance and high water solubility of HNO_3 in comparison to other NO_y species in the atmosphere. It could also be related to a possible high correlation of atmospheric concentration of HNO_3 with those of other airborne NO_x reaction products that are removed from the atmosphere and measured as aqueous NO_3 ion in precipitation.

Model predictions for the continental US (Zhang et al., 2012) suggest approximately 63 % of 2006–2008 NO_x emissions are deposited as NO_y and 45 % as OxN. In the current study, none of the primary NO_x species and only two of the secondary species (HNO_3 and aerosol NO_3) are monitored. Nevertheless, neglecting other sources and sinks, it is possible to compare NO_x emissions density with total OxN deposition to determine the fraction of NO_x emissions deposited as OxN. Using the approach described in Sect. 4.4.1 for oxidized sulfur, approximately 30 % of the NO_x emissions appear to be deposited as OxN during the study period. Although there are hints of a numerically small P1-to-P4 increase in the relative amount of NO_x emissions deposited as OxN, the large relative uncertainty associated with NO_x emissions estimates (Sect. 4.4) precludes a conclusion in this instance. Nevertheless, the strong P1-to-P4 reduction of NO_x emissions (42 %) is accompanied by reduced atmospheric concentration of HNO_3 and OxN as well as $RHNO_3$ (Sects. 3.3 and 4.3), and by increased relative contribution of wet OxN vs. dry OxN (Sect. 4.2).

4.4.3 Wet H^+

In the east the P1-to-P2 reductions in estimated emissions are 21 % for SO_2 and 6 % for NO_x. Concurrent changes in deposition include reductions of 17 % for wet S, 3 % (NS) for both wet OxN and wet NH_4, and 24 % for wet H^+ (not shown). In the absence of sizeable P1-to-P2 changes in NO_x emissions, it appears that P1-to-P2 reductions in SO_2 emissions played a major role in the resulting reductions of both wet S and wet H^+ in the east. P1-to-P3 reductions in estimated SO_2 and NO_x emissions are 35 and 22 %, with corresponding reductions of 22 % in wet S, 12 % in wet OxN, no change in wet NH_4, and 34 % in wet H^+ (SS07b). For P1-to-P4, reductions in estimated SO_2 and NO_x emissions are 50 and 42 %, and corresponding reductions are 32 % for wet S, 29 % for wet OxN, 9 % for wet NH_4, and 47 % for wet H^+ (Fig. 4). Respective P3-to-P4 reductions in estimated SO_2 and NO_x

emissions are 23 and 25 %, with corresponding reductions of 13 % in wet S, 19 % in wet OxN, 9 % in wet NH_4, and 20 % in wet H^+.

Changes in wet NH_4 between P1 and P3 are generally small, variable, and non-significant. Although significant P1-to-P4 reductions in wet NH_4 are also relatively small (≈ 9 %), they occur mainly between P3 and P4. In the east between P1 and P4, with the continuing reduction in SO_2 and NO_x emissions, the fraction of wet S plus wet OxN that could be neutralized on an equivalent basis by wet NH_4 increased by approximately 8 % from 25 % in P1, to 33 % in P4.

Neglecting the relatively small temporal impacts of wet NH_4 (above) and those of other wet cations, examination of the behavior of wet S plus wet OxN (on an equivalent basis) permits rough estimation of the relative contributions of reductions in SO_2 and NO_x emissions to corresponding reductions in wet H^+. Year-round in the east, P1-to-P3 reductions in wet S contribute most (≈ 80 %) of the relative reduction of wet S plus wet OxN associated with reduced wet H^+. Between P1 and P4, this relative contribution diminishes (to ≈ 70 %), and between P3 and P4 the relative contribution of wet S (≈ 55 %) approaches that of wet OxN. This finding illustrates the impact of recent aggressive NO_x emissions controls along with continuing SO_2 controls on wet H^+ and the increasing relative contribution of reductions in NO_x emissions to the significant and substantial reduction of wet H^+ in the eastern US.

5 Summary, conclusions, and recommendations

Data collected in the eastern US between 1990 and 2009 at 34 CASTNET dry monitoring sites and paired NADP wet monitoring sites are examined. A major objective is to evaluate the monitored air quality impacts occurring between 1990 and 2009 that are associated with concurrent legislatively mandated changes in emissions. Four 5-year periods (P1, P2, P3, and P4) are considered. Period-to-period changes in selected pollutant metrics are examined, focusing on P1-to-P4 changes. Data are composed from reported weekly measurements into period–site–season means. These means, computed for atmospheric concentration, Vd, PR, and dry, wet, and total deposition, are used to examine differences between 5-year periods for seasons, sites, and predefined regional groupings of sites. The approach to data analysis uses the mean squared error derived from analysis of variance of mean estimates for each pollutant metric to examine differences in the monitoring data and metrics derived from them.

Estimated SO_2 emissions for P4 are 50 % lower than for P1. This is accompanied in each regional site grouping in each season and over all seasons by significant reductions in atmospheric SO_2 concentration and dry deposition, atmospheric aerosol SO_4 concentration, atmospheric S concentration and dry deposition, wet S (except in winter), and total S. For atmospheric SO_2 concentration and dry deposition, the numerically largest significant seasonal absolute reductions usually occur in winter when atmospheric SO_2 concentration is at its seasonal maximum. Analogous behavior occurs in summer for atmospheric aerosol SO_4 concentration, dry SO_4, and wet S, when atmospheric aerosol SO_4 concentration is at its seasonal maximum. In the east, significant reductions of 48 %, 33 %, and 45 % for atmospheric concentration of SO_2, aerosol SO_4 and atmospheric S, and of 49 %, 32 %, and 40 % for dry, wet, and total deposition of atmospheric S are associated with the 50 % P1-to-P4 reduction in estimated SO_2 emissions. Consistent with earlier findings (SS07b), results suggest that at the current scale, the responses of both atmospheric SO_2 concentration and dry deposition to changes in SO_2 emissions are close to 1 : 1 and the relationship between changes in the concentration of the secondary reaction product, aerosol SO_4, and that of the primary pollutant, SO_2, appears to be less than 1 : 1. The strong P1-to-P4 reduction of SO_2 emissions (50 %) is accompanied by increased apparent conversion of SO_2 to aerosol SO_4, possible increased relative contribution of wet vs. dry deposition as a sink for S, increased fraction of deposited S emissions, and decreased fraction of exported S emissions.

In the east, significant P1-to-P4 reductions of 34 %, 8 %, and 24 % for atmospheric concentration of HNO_3, aerosol NO_3 and OxN, and of 34 %, 29 %, and 31 % for dry, wet, and total deposition of OxN are associated with the 42 % reduction in estimated NO_x emissions. Atmospheric aerosol NO_3 concentration in the east displays a significant P1-to-P3 increase (11 %), with the numerically strongest seasonal relative increase (31 %) in winter (SS07b). Recent aggressive reductions of NO_x emissions have been accompanied by significant P1-to-P4 and P3-to-P4 reductions of 8 and 17 % in atmospheric aerosol NO_3 concentration over all seasons. In addition, the smaller P1-to-P4 wintertime increase in atmospheric aerosol NO_3 concentration (i.e., 12 % vs. 31 % for P1-to-P3) and the P3-to-P4 wintertime reduction of 14 % suggest that recent continuing NO_x emissions controls are having a desirable impact. Over all seasons the numerically largest absolute and relative reductions in atmospheric HNO_3 concentration and dry deposition, atmospheric OxN concentration and dry deposition, and total OxN generally occur in the northeast (the geographical region with the highest P1 NO_x emissions density), and seasonally they tend to occur there in summer. In the east, coincident timing and location suggest that aggressive summertime NO_x emissions reductions by EGU sources contributed substantially to this observed behavior. The strong P1-to-P4 reduction of NO_x emissions (42 %) is accompanied by reduced atmospheric concentration of HNO_3 relative to OxN, and increased contribution of wet OxN relative to dry OxN.

Estimated annual 1990 to 2009 NH_3 emissions are relatively constant, ranging between 3.5 and 3.9 $\mathrm{Tg\,yr^{-1}}$ (Xing et al., 2013). However, this is not confirmed through monitoring in the current study, because only the atmospheric concentration of the secondary reduced nitrogen species, aerosol NH_4, is monitored. In the east, both atmospheric aerosol NH_4 concentration and dry deposition show significant P1-to-P4 reductions (i.e., 26 and 22 %). The numerically largest absolute and relative reductions of atmospheric aerosol NH_4 concentration and dry deposition tend to occur regionally in the midwest and northeast and seasonally in the summer (when atmospheric aerosol SO_4 concentration is at its seasonal maximum and is also experiencing its largest reductions). Although showing a significant (9 %) P1-to-P4 reduction over all in the east, wet NH_4 shows changes at the regional and seasonal scales that are usually not significant. Since the magnitude of wet NH_4 is over seven times larger than dry deposition, the resulting reduction in total NH_4 in the east (11 %) is similar to that of wet NH_4.

The atmospheric concentration of N, the sum of monitored oxidized and reduced nitrogen species, is dominated in the east by aerosol NH_4 ($\approx$ 67 %) with smaller contributions from HNO_3 ($\approx$ 19 %) and aerosol NO_3 ($\approx$ 14 %). However, a high Vd permits HNO_3 to dominate dry deposition of N ($\approx$ 75 %). Both the atmospheric concentration and dry deposition of N show significant overall P1-to-P4 reductions (26 and 32 %) which tend to be seasonally higher in summer. Wet deposition of OxN and NH_4 are fairly comparable, and their sum (wet N) dominates total N ($\approx$ 75 %). The overall P1-to-P4 relative reductions of wet N and total N in the east are 20 and 24 %, with the strongest reductions in summer and in the northeast.

In the east, a 47 % reduction in wet deposition of H^+ ion is associated with P1-to-P4 reductions of 50 and 42 % in SO_2 and NO_x emissions. The relative contributions of reduced NO_x vs. SO_2 emissions have increased over time, until currently (P3-to-P4), they are almost equal. Thus, recent aggressive reductions of NO_x emissions along with continuing reductions of SO_2 emissions appear to contribute similarly to the significant and substantial reduction of wet deposition of H^+ ion in the eastern US.

Although both atmospheric O_3 concentration and dry deposition in the east show significant summertime P1-to-P4 reductions of 12 % each, significant wintertime respective increases of 9 and 19 % lead to overall significant reductions of 4 % each. The numerically largest seasonal and regional reductions of both atmospheric O_3 concentration and dry deposition (17 and 15 %) occur in summer in the northeast, coinciding with aggressive O_3-season NO_x emissions controls during P3 and P4 in the region and upwind in the east.

Although conditions in the east permitting the formation of aerosol NO_3 may be limited by the availability of NH_3, this appears to be diminishing over time. Increasing NI between P1 and P4 suggests that an acidic aerosol exists in the east, but is approaching neutralization due to increased relative availability of NH_3 associated with reductions of aerosol SO_4 concentration. Widespread wintertime numerical increases in the atmospheric concentrations of both aerosol NO_3 and CASTNET PM are present between P1 and P3, despite reductions in estimated emissions of both SO_2 and NO_x (SS07b). Currently, this behavior appears to be largely reversed, and this reversal is associated with continuing reductions of SO_2 and NO_x emissions between P3 and P4. Our findings suggest that additional P3-to-P4 reductions in emissions of SO_2, and especially NO_x, have made progress in altering the chemical regime of the wintertime eastern US atmosphere so that future emissions reductions and their resulting reductions in aerosol concentrations may no longer be accompanied by sub-linear changes (or actual increases) in CASTNET PM.

Monitoring data for several atmospheric species not collected by CASTNET, including NH_3, NO, NO_2, PAN, other oxidized organic nitrogen species, and NO_y, as well as aerosol size distributions would have facilitated data analysis and interpretation. It is recommended that addition of these determinations be considered in future monitoring network upgrades. Uncertainties in estimates of many species' deposition velocities and emissions (especially NO_x) argue strongly for their continued improvement.

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