Impact of Sulfur Dioxide (SO$_2$) and Nitrogen Oxide (NO$_x$) Emissions Reductions on ACIDIC DEPOSITION in the United States

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Background

As extensively described in A&WMA’s 2007 Critical Review on the history of the National Ambient Air Quality Standards (NAAQS), regulations have been promulgated in the United States to address the adverse impacts of air pollution on human health and the environment since the original Clean Air Act (CAA) of 1963. The 1990 CAA Amendments (CAAA) specifically sought to limit the adverse impact of acidic deposition through control of emissions of SO$_2$ and NO$_x$. Title IV of the 1990 CAAA set sulfur dioxide (SO$_2$) emissions limits to reduce 1980-level air emissions by 9.1 teragrams (Tg, $10^{12}$ g) or 10 million short tons by the year 2000. Title IV also regulated NO$_x$ emissions from stationary sources, and Title II regulated NO$_x$ mobile source emissions. The U.S. EPA’s Acid Rain and related programs established subsequent rules to further limit emissions of SO$_2$ and NO$_x$ from stationary and mobile sources to improve air quality and public health. The current Cross-State Air Pollution Rule (CSAPR) requires 23 central and Midwestern U.S. states to significantly improve air quality by reducing stationary source emissions. Such controls include summertime NO$_x$ reductions to mitigate ozone production and annual SO$_2$ emissions reductions to limit fine particle formation. Phase I of CSAPR will be implemented in 2015.

Trends in Atmospheric Emissions of SO$_2$ and NO$_x$

The U.S. EPA provides air emissions data (1970–2014) through the National Emissions Inventory (NEI). These data show that significant decreases in SO$_2$ and NO$_x$ have occurred from 1970 to present in response to rules and legislation targeting emissions of these species (Figure 1).

Figure 1. Annual emissions of SO$_2$ and NO$_x$, reported in the U.S. EPA’s National Emissions Inventory (NEI).

Note: Estimated emissions from wildfires are not included. Significant regulatory controls affecting stationary-source SO$_2$ air emissions (red text) and NO$_x$ emissions (blue text) are indicated at the year of implementation.
SO₂ emissions have decreased from over 25 Tg/yr in 1970 to less than 5 Tg in 2014. NOₓ emissions, originally estimated to be less than SO₂ emissions in 1970 (~24 Tg/yr), exceeded SO₂ emissions by over a 2:1 ratio in 2014 (~11 Tg/yr). Figure 1 includes stationary-source regulatory controls on SO₂ air emissions (red text) and NOₓ air emissions (blue text) at the year of implementation. These regulatory controls include Phases I and II of the 1990 CAAA, and the Clean Air Interstate Rule (CAIR); some of these programs provided incentives for sources to reduce emissions before the compliance dates shown.5,8 Additional mobile-source emissions regulations (e.g., Tier I emissions, Tier II emissions, and low-sulfur fuel standards) are not shown in the figure but are detailed elsewhere by the U.S. EPA.5,8

Monitoring of Atmospheric SO₂ and NOₓ Trends

There are several national-level monitoring networks that measure long-term ambient concentrations of criteria air pollutants for compliance with the CAAA including the State and Local Air Monitoring Stations (SLAMS) and the related National Air Monitoring Stations (NAMS) networks.9 Monitoring of precipitation (i.e., rain and snow) chemistry also provides an indicator of overall air quality, as precipitation readily scavenges the airborne gases and particles generated by emissions. Dry deposition monitoring of particles and gases, including estimates of their removal fluxes using atmospheric models, provides estimates of total deposition of pollutants and their overall removal from the atmosphere.

The National Atmospheric Deposition Program (NADP) has measured the concentrations of pollutants in precipitation samples since 1978 and related air-quality parameters to characterize the chemical climate of the U.S. and its temporal and spatial trends.10 The NADP is a coordinated research project supported by over 150 cooperating agencies which sponsor one or more individual monitoring stations, currently comprising over

Figure 2. Three-year (1984–1986, 2012–2014) precipitation volume-weighted mean concentrations of SO₄²⁻ (top) and NO₃⁻ (bottom) ions in NADP/NTN precipitation samples as hydrogen ion microequivalents per liter (µeq/L).10 Colors between station locations represent an Inverse-Distance-Weighting (IDW) interpolation. All valid samples were included for 139 sites meeting completeness criteria during both time periods. Sites within 100 km of oceans were corrected for sea-salt sulfate concentrations.15
350 locations in the U.S. (and its territories), Canada, Argentina, and Taiwan. The NADP consists of the following five networks:

- **National Trends Network (NTN)** — Established in 1978; weekly concentrations and wet deposition fluxes of sulfate (SO$_4^{2-}$), nitrate (NO$_3^-$), chloride (Cl$^-$), bromide (Br$^-$), ammonium (NH$_4^+$), orthophosphate (PO$_4^{3-}$), calcium (Ca$^{2+}$), magnesium (Mg$^{2+}$), potassium (K$^+$), and sodium (Na$^+$) ions, as well as pH and specific conductivity.

- **Atmospheric Integrated Research Monitoring Network (AIRMoN)** — Established in 1992; event-based measurements of the same species as NTN.

- **Mercury Deposition Network (MDN)** — Established in 1995; weekly concentrations and wet deposition fluxes of mercury.

- **Atmospheric Mercury Network (AMNet)** — Established in 2009; gaseous ambient concentrations of mercury fractions.

- **Ammonia Monitoring Network (AMoN)** — Established in 2010; gaseous ambient concentrations of ammonia.

Dry deposition monitoring in the U.S. is provided by the Clean Air Status and Trends Network (CASTNET). More information on CASTNET is available at http://epa.gov/CASTNET. Together, wet and dry deposition monitoring networks complement the SLAMS and NAMS networks in evaluating overall air pollutant trends in the U.S.

### Impacts

**Effects of Emissions Regulations on Sulfate (SO$_4^{2-}$) and Nitrate (NO$_3^-$)**

**Acidic Wet Deposition**

SO$_2$ and NO$_x$ air emissions are oxidized in the atmosphere, and are wet deposited as acidic SO$_4^{2-}$ and NO$_3^-$ ions in precipitation, respectively. Reductions of U.S. SO$_2$ and NO$_x$ air emissions have had a direct and quantifiable impact on SO$_4^{2-}$ and NO$_3^-$ wet deposition. Three-year precipitation volume-weighted mean concentrations of SO$_4^{2-}$ and NO$_3^-$ ion concentrations as microequivalents per liter (µeq/L) are shown for two time periods (1984–1986 and 2012–2014) in Figure 2. The maps demonstrate that sulfate and nitrate concentrations are decreasing, consistent with emissions reductions (Figure 1). Median SO$_4^{2-}$ concentrations for the 139 stations shown in Figure 2 decreased from 28.6 µeq/L in 1984–1986 to 11.8 µeq/L in the 2012–2014 period, representing a 59% decrease. Median NO$_3^-$ concentrations decreased from 14.7 µeq/L to 11.5 µeq/L during the same period, a decrease of 22%. The NADP provides a time-series animation of SO$_4^{2-}$ and NO$_3^-$ concentrations and wet deposition fluxes at http://nadp.isws.illinois.edu/data/animaps.aspx.

The larger magnitude emissions reduction in SO$_4^{2-}$

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*a. When evaluating the acidification potential of sulfate and nitrate ions, each molar unit concentration of SO$_4^{2-}$ contributes two hydrogen ion equivalents, and NO$_3^-$ contributes one hydrogen ion equivalent.*
relative to NO₃⁻ is reflected in the shift in the relative equivalents ratio of these two species between the three-year periods 1984–1986 and 2012–2014 (Figure 3). In 1984–1986, the region where the SO₄²⁻ to NO₃⁻ equivalents ratio (SO₄²⁻/NO₃⁻) was greater than 2:1 represented one-third of the total area of the continental U.S. By 2012–2014, the region represented a very small area of the continental U.S. In contrast, the region where SO₄²⁻/NO₃⁻ was less than 1:1 represented only a small area along the West Coast in 1984–1986. By the 2012–2014 period, the region where SO₄²⁻/NO₃⁻ was less than 1:1 represented more than half of the continental U.S., principally in western states. This indicates that NO₃⁻ wet deposition exceeds SO₄²⁻ deposition in much of the continental U.S. for its acidification impacts.

Quantifying Ecosystem Impacts: Total Deposition and Critical Loads

In 2011, the NADP formed the Total Deposition Science Committee (TDEP) to improve estimates of atmospheric deposition through integration of measured and modeled wet, dry, and total deposition of sulfur, nitrogen and other species of concern (e.g., mercury). This committee has produced a series of maps representing the total deposition of sulfur and nitrogen species, available at http://nadp.isws.illinois.edu/committees/tdep/tdepmaps/, as well as published in print. These maps provide estimates on the total loading of sulfur and nitrogen pollutants. Total deposition provides data for ecological assessments, including evaluation of critical loads.

The critical load represents the threshold at which air pollution deposition results in a response in sensitive resources or ecosystems. Critical loads can be developed for various ecosystem responses, including impacts on aquatic systems, spread of invasive species, changes in soil chemistry, and stream acidification. For ecosystems currently experiencing damage from air pollution, critical loads help determine deposition reductions required for ecosystem recovery. In areas where critical loads are not exceeded, the levels inform land management and policy decisions regarding appropriate air quality standards to protect ecosystems. A series of critical loads maps was recently published for the U.S.

Future Directions
Development of NOₓ/SOₓ Secondary Standards

The CAA requires the U.S. EPA to set primary and secondary National Ambient Air Quality Standards (NAAQS) for the six criteria pollutants (including NOₓ and SO₂), and periodically review them. Primary NAAQS are established to protect human health and sensitive populations. Secondary NAAQS protect ecosystems and human welfare. As the U.S. EPA reviews secondary NOₓ/SOₓ NAAQS, the objective is to develop a framework of standards that recognizes the interactions between NOₓ and SOₓ as they deposit to sensitive ecosystems. This is consistent with the CAA’s requirements to protect human health and public welfare, as well as impacts on sensitive ecosystems (e.g., acidic

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deposition). The U.S. EPA is moving towards a multi-pollutant regional approach, recognizing that NAAQS-level controls do not take into account regional variations, including atmospheric and topographic variables as well as the location of sensitive ecosystems.14

References