



Air Quality Related Values (AQRVs) for Mid-Atlantic Network (MIDN) Parks

Effects from Ozone; Visibility Reducing Particles; and Atmospheric Deposition of Acids, Nutrients and Toxics

Natural Resource Report NPS/MIDN/NRR—2016/1163



ON THE COVER

Photograph of air quality related values within various National Park units. Wildflowers, clear views, aquatic species, and lichens may all be threatened by air pollution.

Photographs courtesy of the National Park Service

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Summary

This report describes the Air Quality Related Values (AQRVs) of the Mid-Atlantic Network (MIDN). AQRVs are those resources sensitive to air quality and include streams, lakes, soils, vegetation, fish and wildlife, and visibility. The MIDN parks that are included in the National Park Service (NPS) Inventory and Monitoring (I&M) Program, and discussed in this report, are Appomattox Court House National Historical Park (APCO), Booker T. Washington National Monument (BOWA), Eisenhower National Historic Site (EISE), Fredericksburg and Spotsylvania National Military Park (FRSP), Gettysburg National Military Park (GETT), Hopewell Furnace National Historic Site (HOFU), Petersburg National Battlefield (PETE), Richmond National Battlefield Park (RICH), Shenandoah National Park (SHEN), and Valley Forge National Historical Park (VAFO). SHEN is designated as Class I, giving it a heightened level of protection against harm caused by poor air quality under the Clean Air Act (CAA). It is the only park in the network that is larger than 100 mi² (260 km²). Data with which to assess potential air pollution effects within MIDN parks are mainly available for SHEN. Other parks are discussed here in considerably less detail.

Sullivan et al. (2011a, 2011b) and Kohut (2007a) conducted risk assessments for acidification, eutrophication, and ozone (O₃) for the MIDN parks; their results are described in this report. This report also describes air pollutant emissions and air quality, and their effects on AQRVs in the MIDN. The primary pollutants likely to affect AQRVs include nitrogen (N) and sulfur (S) compounds (nitrate [NO₃⁻], ammonium [NH₄⁺], and sulfate [SO₄²⁻]); ground-level O₃; haze-causing particles; and airborne toxics. Background for this section can be found in “Air quality related values (AQRVs) in national parks: Effects from ozone; visibility reducing particles; and atmospheric deposition of acids, nutrients and toxics.” (Sullivan 2016).

The MIDN parks are located in relatively remote areas. They receive air pollutants from regional and local emissions sources, including large power plants, urban areas, agriculture, and oil and gas development. Air pollution is an important stressor to natural resources in MIDN parks.

The major source areas of atmospheric emissions of S and N that impact sensitive resources within SHEN and surrounding areas within the MIDN are located in the Ohio River Valley, northeastern West Virginia, southwestern Pennsylvania, and central and eastern Virginia, based on simulations using the atmospheric transport model Regional Acid Deposition Model (RADM; Sullivan et al. 2003). There are many large urban centers within a 300-mile radius of the network boundary, including several (Baltimore, Washington, DC, New York, Richmond, and Philadelphia) relatively close to some of the network parks.

Sulfur and, to a lesser extent N, pollutants can cause acidification of streams, lakes, and soils in MIDN parks. Sulfur deposition in the MIDN network peaked sometime during the 1970s or early 1980s and has been declining steadily since then. Nitrogen pollutants can also cause undesirable enrichment of natural ecosystems, leading to changes in plant species diversity and soil nutrient cycling. Nitrogen deposition in the MIDN region was high throughout the 1980s and 1990s, but has declined since 2000. Wet deposition collected at 29 national park locations was reported by the National Park Service (NPS; 2010). Most monitored sites showed statistically significant ($p \leq 0.05$)

decreases in concentrations of SO_4^{2-} in wet deposition between about 1989 and 2008. One of the largest decreasing trends was reported for SHEN. Sulfur and N oxide (NO_x) deposition are expected to continue to decrease as the Acid Rain Program and other air quality management programs are fully implemented (Burns et al. 2011).

Airborne contaminants, including Hg, can accumulate in food webs, reaching toxic levels in top predators. Wet Hg deposition is relatively high in the MIDN. Three-year means of annual Hg concentration in rain and snow were reported by NPS (2010) for 13 national parks that had at least two years of valid data during the period 2006-2008. SHEN was among the five parks having highest Hg concentration in precipitation. Concentrations of Hg in precipitation were unchanged over the period 2000-2009 (NPS-ARD 2013).

Research on the effects of atmospheric deposition on sensitive park receptors in the MIDN has focused almost exclusively on SHEN. This park has received some of the highest levels of air pollution (including S, N, and O_3) of any national park studied. Over 20 years of scientific research and monitoring in SHEN have shown that, despite some recent improvements, the park's sensitive scenic, vegetative, and aquatic resources remain degraded by human-made air pollution.

The most thoroughly studied air pollution impact in SHEN has been stream acidification. Aquatic biota in the MIDN have been affected by acidification at virtually all levels of the food web. Effects have been clearly documented for fish, aquatic insects, other invertebrates, and algae. Researchers have drawn the following conclusions based on model simulations and review of available data on aquatic acidification effects in SHEN (Shenandoah National Park 2007):

- The vast majority of low-acid neutralizing capacity (ANC) sampled streams were underlain by the siliceous geologic sensitivity class. Modeled streams on siliciclastic (silica-based) bedrock showed critical S deposition loads to protect against acidification to ANC of 50 $\mu\text{eq/L}$ in the year 2100 ranging from less than 0 kg S/ha/yr (target ANC not attainable, even with no future acidic deposition) to 6 kg S/ha/yr. Of the 14 modeled park streams, none had simulated pre-industrial streamwater ANC less than 50 $\mu\text{eq/L}$, suggesting that these streams may have supported a greater variety of aquatic fauna prior to the Industrial Revolution.
- Almost half of the siliciclastic streams in a 1992 survey of small subwatersheds in SHEN were chronically acidic (ANC < 0 $\mu\text{eq/L}$). The balance of siliciclastic streams had ANC in the episodically acidic range (having chronic ANC between 0 and 20 $\mu\text{eq/L}$). These thresholds were developed for brook trout (*Salvelinus fontinalis*), which is considered the most acid tolerant fish species in the park. Species which are more acid-sensitive, such as blacknose dace (*Rhinichthys atratulus*) and some mayfly (Ephemeroptera) and caddisfly (Trichoptera) species, likely have higher suitable ANC ranges than brook trout. Generally, ANC values greater than 20 to 50 $\mu\text{eq/L}$ should support greater diversity and larger populations of aquatic fauna.
- Episodic acidification of park streams can be attributed to both acidic deposition and natural processes, and it is superimposed on baseflow chemistry that is more acidic than pre-industrial conditions. Episodic stream ANC values are generally about 20% lower than baseflow values.

- Park streamwater chemistry is showing some signs of ANC recovery in recent years in response to decreased sulfur deposition, whereas streamwater chemistry within the larger western Virginia region is not.
- Acidic episodes in low ANC park streams killed young brook trout and adult blacknose dace in field bioassays.
- Modeling results suggested that park streams that occur on siliciclastic bedrock have generally lost one or two species, and some streams may have lost up to four species, of fish in response to acidic deposition.
- Low ANC park streams generally have lower fish species richness, lower population density, poorer blacknose dace condition, fewer age classes, smaller sizes, and lower field bioassay survival than higher ANC streams.
- Higher ANC streams generally have greater numbers of families and numbers of individuals than low-ANC streams in each of the important benthic insect orders: mayflies, stoneflies (Plecoptera), and caddisflies.

SHEN was ranked very high among parks by Sullivan et al. (2011b) in acid Pollutant Exposure and Ecosystem Sensitivity to acidification, near the top among all I&M parks. This was due to both the presence of nearby pollution sources and substantial acid-sensitive resources in SHEN.

Because of watershed S retention, soils and surface waters of the MIDN and southward throughout the southern Appalachian Mountain region have not yet realized the full effects of decades of elevated S deposition. Sulfur retention on soils will likely continue to decrease in the future, resulting in further losses of stream ANC, even under moderately decreasing levels of S deposition.

Ozone pollution can harm human health, reduce plant growth, and cause visible injury to foliage. Two of the MIDN parks, HOFU and VAFO, are in counties designated by the U.S. Environmental Protection Agency (EPA) as nonattainment for the O₃ standard because of high atmospheric O₃ levels. Of all monitored eastern national parks, the air in SHEN has among the highest measured concentrations of O₃. During the 1990s, O₃ levels in SHEN generally showed an increasing trend. Over the following several years, O₃ concentrations stabilized. The probability of injury to plant foliage at SHEN was judged to be greatest during years when O₃ levels exceeded thresholds and soil moisture was high enough so that it was unlikely that there were long-term constraints on O₃ uptake into plant foliage. Ground-level O₃ causes visible foliar symptoms on several plant species in SHEN, including but not limited to milkweed (*Asclepias* spp.), black cherry (*Prunus serotina*), yellow poplar (*Liriodendron tulipifera*), and white ash (*Fraxinus americana*). Modeling results suggested that ground-level O₃ exposures about 15% less than 1997 through 1999 ambient levels would be needed to protect against changes in white ash growth and species composition shifts in the park's forests. From 2000-2009, O₃ air concentrations decreased significantly at SHEN (NPS 2013), but there was no significant increase or decrease in O₃ near FRSP and RICH, the two other network parks with nearby O₃ monitors (NPS 2013).

Haze levels are high throughout the eastern United States. Visibility is degraded by haze in SHEN, detracting from visitor enjoyment of scenic vistas, especially along Skyline Drive, which is designated as a Virginia State Scenic Highway, and the Appalachian National Scenic Trail, which passes through the park. Changes in visibility over time in this park are mainly caused by changes in the concentration of particles of ammonium sulfate ((NH₄)₂SO₄) in the atmosphere.

NPS (2010) reported long-term trends in annual average haze on the clearest and haziest 20% of days at monitoring sites in 29 national parks. The steepest declines (-0.18 to -0.20 dv/yr) on the clearest days were reported for SHEN, Acadia National Park in Maine, and Washington DC. Ten parks showed statistically significant decreases in dv on the haziest days, with the second steepest decline reported for SHEN (-0.27 dv/yr), based on 18 years of data. More recently (2000-2009), haze measurements continued to decrease significantly in SHEN on the clearest days, but there was no significant trend on the haziest days (NPS 2013).

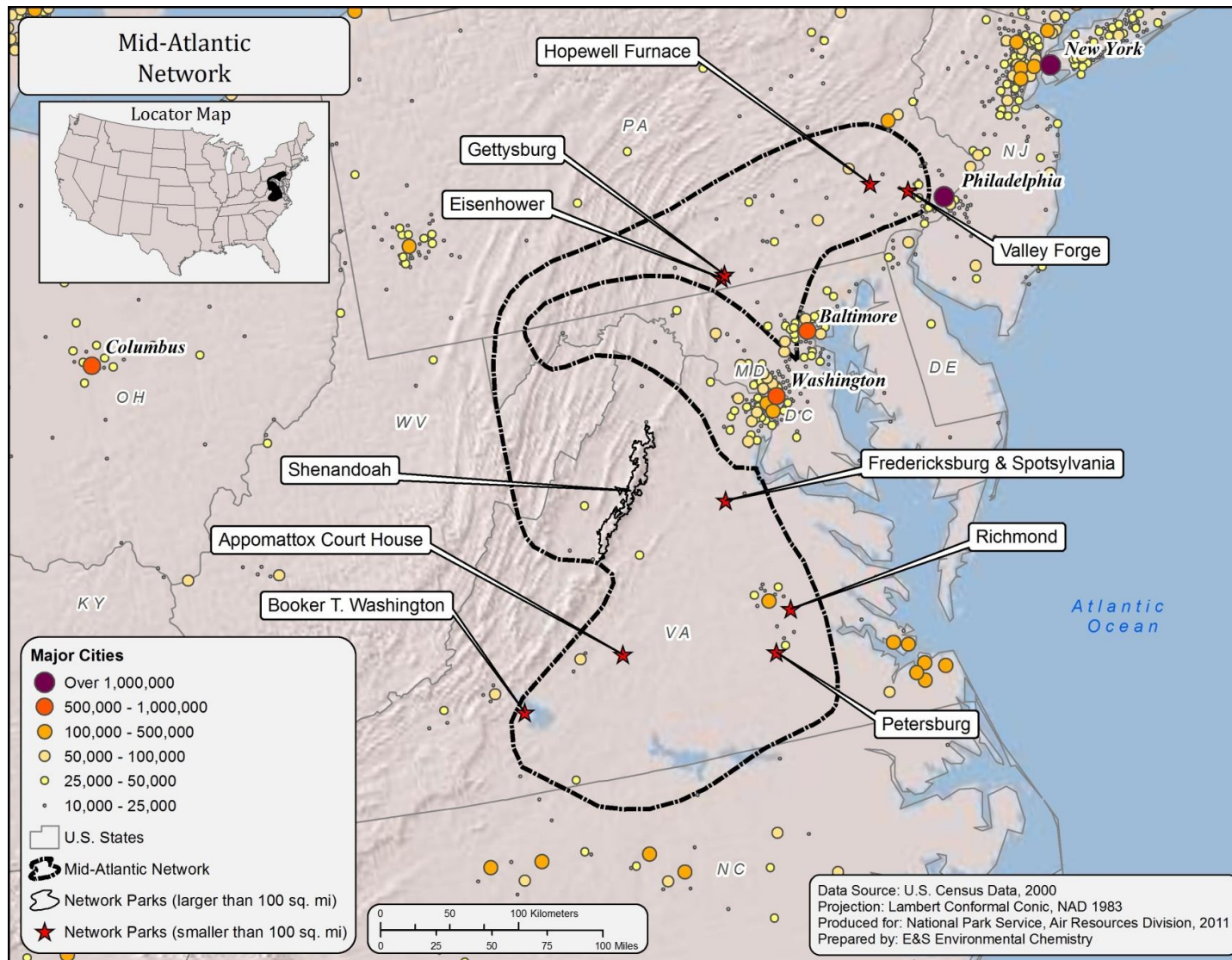
Background

The Mid-Atlantic Network (MIDN) region consists of portions of the Blue Ridge, Ridge and Valley, Piedmont, Coastal Plain, and Northern Piedmont ecoregions, between the Virginia-North Carolina border and southern Pennsylvania. There is only one park in the MIDN that is larger than 100 square miles: Shenandoah National Park (SHEN). Larger parks generally have more available data with which to evaluate air pollution sensitivities and effects. In addition, the larger parks generally contain more extensive resources in need of protection against the adverse impacts of air pollution. There are also nine smaller parks: Appomattox Court House National Historical Park (APCO), Booker T. Washington National Monument (BOWA), Eisenhower National Historic Site (EISE), Fredericksburg and Spotsylvania National Military Park (FRSP), Gettysburg National Military Park (GETT), Hopewell Furnace National Historic Site (HOFU), Petersburg National Battlefield (PETE), Richmond National Battlefield Park (RICH), and Valley Forge National Historical Park (VAFO).

Map 1 shows the network boundary and the location of each national park, along with human population centers around the network that have more than 10,000 people. There are no urban centers within the MIDN that are larger than 500,000 people. However, there are many large urban centers within a 300-mile radius of the network boundary, and others close to the network parks, including Baltimore, Washington, DC, New York, Richmond, and Philadelphia.

Atmospheric Emissions and Deposition

The major source areas of atmospheric emissions of sulfur (S) and nitrogen (N) that impact sensitive resources within SHEN (and presumably many of the other MIDN parks) have been shown to be located in the Ohio River Valley, northeastern West Virginia, southwestern Pennsylvania, and central and eastern Virginia, based on simulations using the Regional Acid Deposition Model



Map 1. Network boundary and locations of parks and population centers greater than 10,000 people around the MIDN.

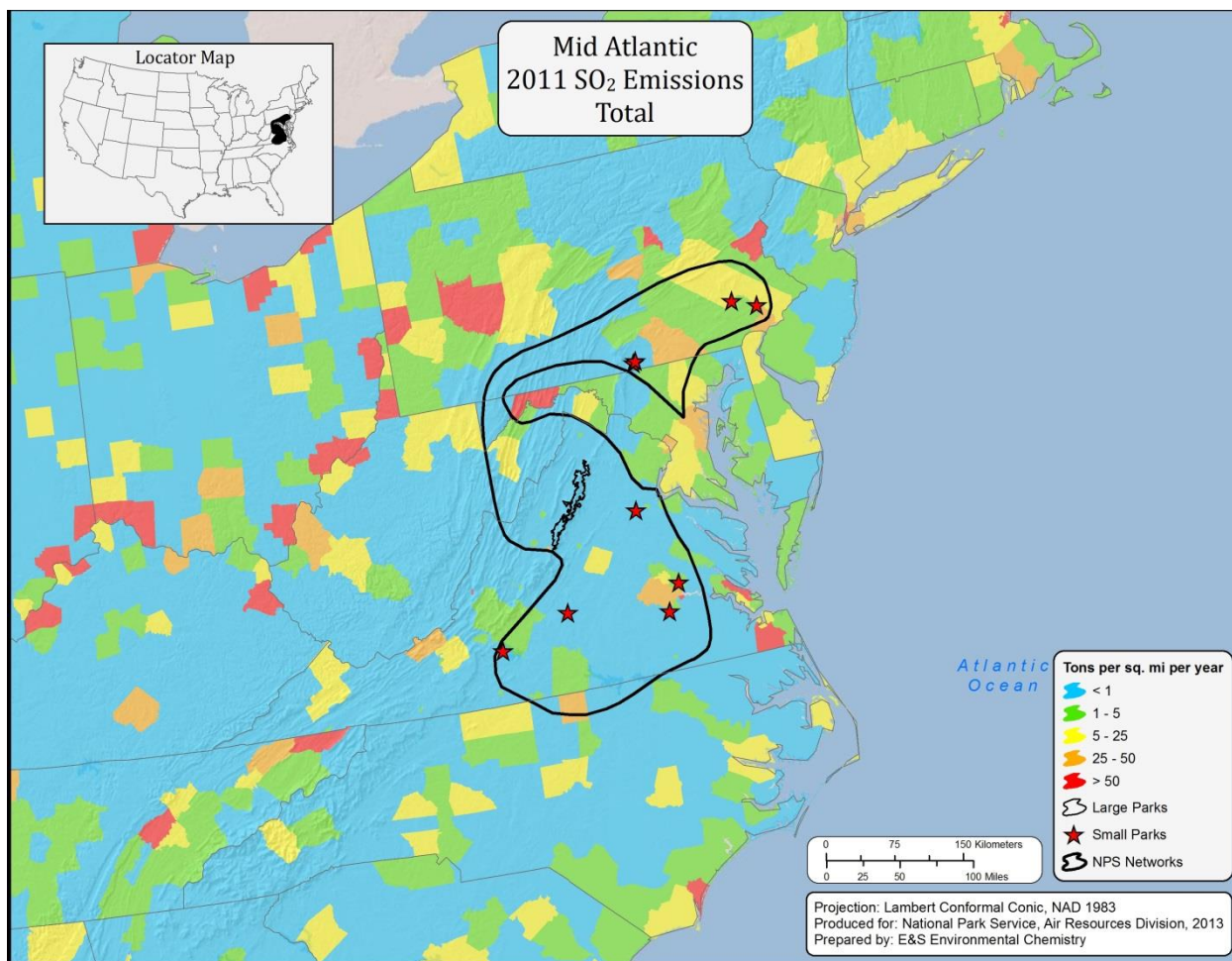
(RADM; Sullivan et al. 2003). County-level SO₂ emissions within the MIDN in 2002, summarized by Sullivan et al. (2011b), ranged from less than 1 to greater than 100 tons per square mile per year (tons/mi²/yr) (Sullivan et al. 2011b). In most counties within the network region, SO₂ emissions were less than 20 tons/mi²/yr, with only a few counties exceeding this amount. Although most point sources of S within the MIDN were less than 5,000 tons per year, there were several sources of greater magnitude, one larger than 40,000 tons per year. There were also numerous large SO₂ point sources to the northwest of the network. Although emissions of SO₂ upwind from SHEN have been high, they have been gradually decreasing since the early 1980s.

Annual county-level N emissions within the MIDN in 2002 ranged from less than 1 ton/mi²/yr to more than 100 tons/mi²/yr. In general, N emissions were between 1 and 20 tons/mi²/yr, but there were several counties with higher N emissions, in the range of 20 to 50 tons/mi²/yr or more. There were relatively few substantial (larger than 1,000 tons per year) N point sources within this network, but there were a number of point sources of oxidized N (NO_x) that were larger than 5,000 tons per year just to the west of the network boundary (Sullivan et al. 2011b). Emissions of N were relatively constant throughout the 1980s and 1990s, but began to decline in about 2000.

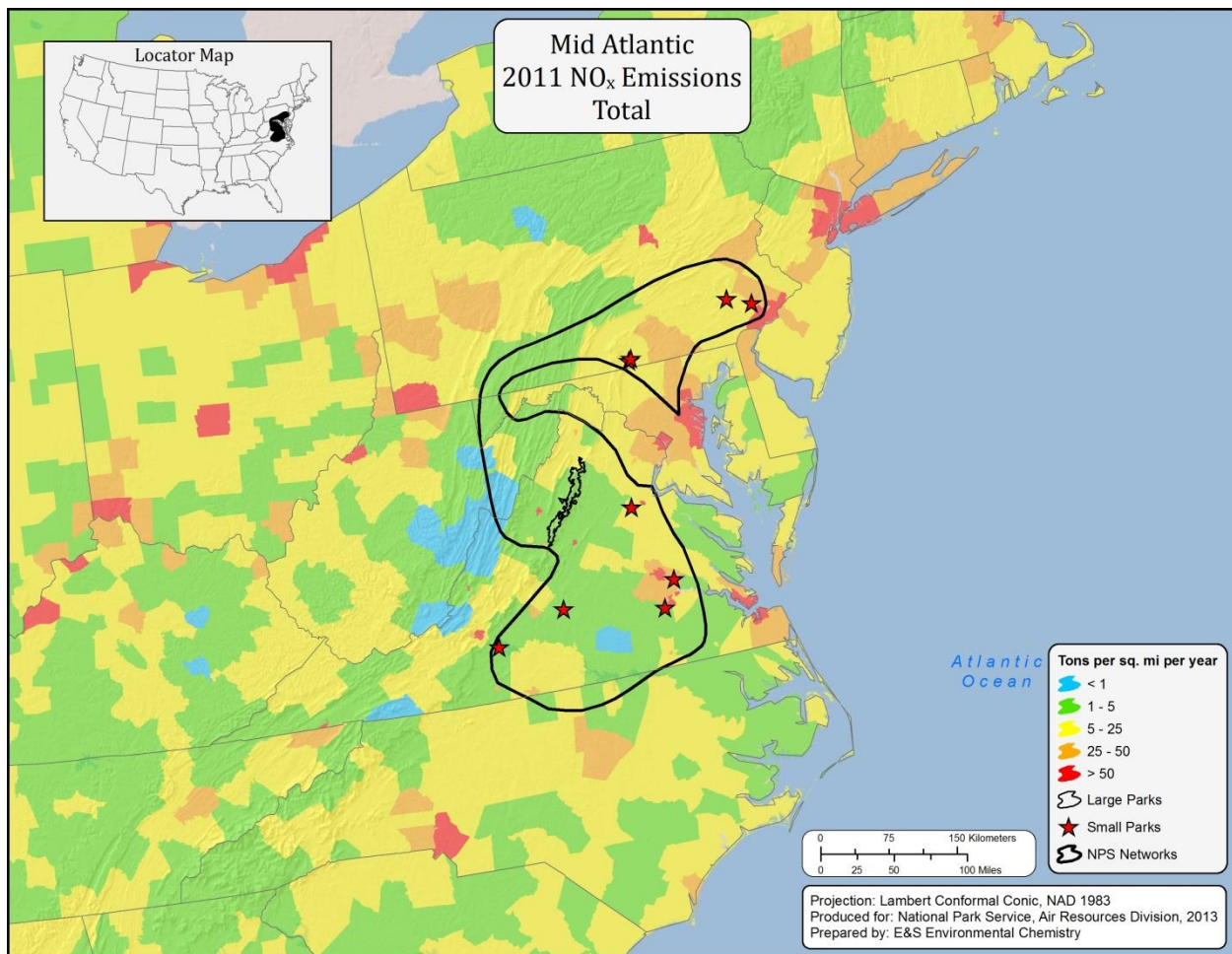
County-level emissions near MIDN, based on data from the EPA's National Emissions Inventory (NEI) during a recent time period (2011), are depicted in Maps 2 through 4 for SO₂, NO_x, and reduced N (NH₃), respectively. Many counties to the west of MIDN parks had relatively high SO₂ emissions (> 50 tons/mi²/yr; Map 2). Spatial patterns in NO_x emissions near the MIDN parks were generally higher than SO₂ emissions (Map 3). Emissions of NH₃ near MIDN parks were somewhat lower, with most counties showing emissions levels below 8 tons/mi²/yr (Map 4).

Total S deposition within the MIDN region ranged from as low as 5 to 10 kg S/ha/yr to greater than 30 kg S/ha/yr in 2002 (Sullivan et al. 2011b). The highest S deposition values within the network occurred to the west and north of SHEN, around GETT and EISE. Sulfur deposition in SHEN peaked sometime during the 1970s or early 1980s and has been declining steadily since then (Figure 1). Total N deposition within the network in 2002 ranged from as low as 5 to 10 kg N/ha/yr to greater than 15 kg N/ha/yr. Estimated total N deposition throughout much of the network, including most of SHEN, was in the range of 10 to 15 kg N/ha/yr.

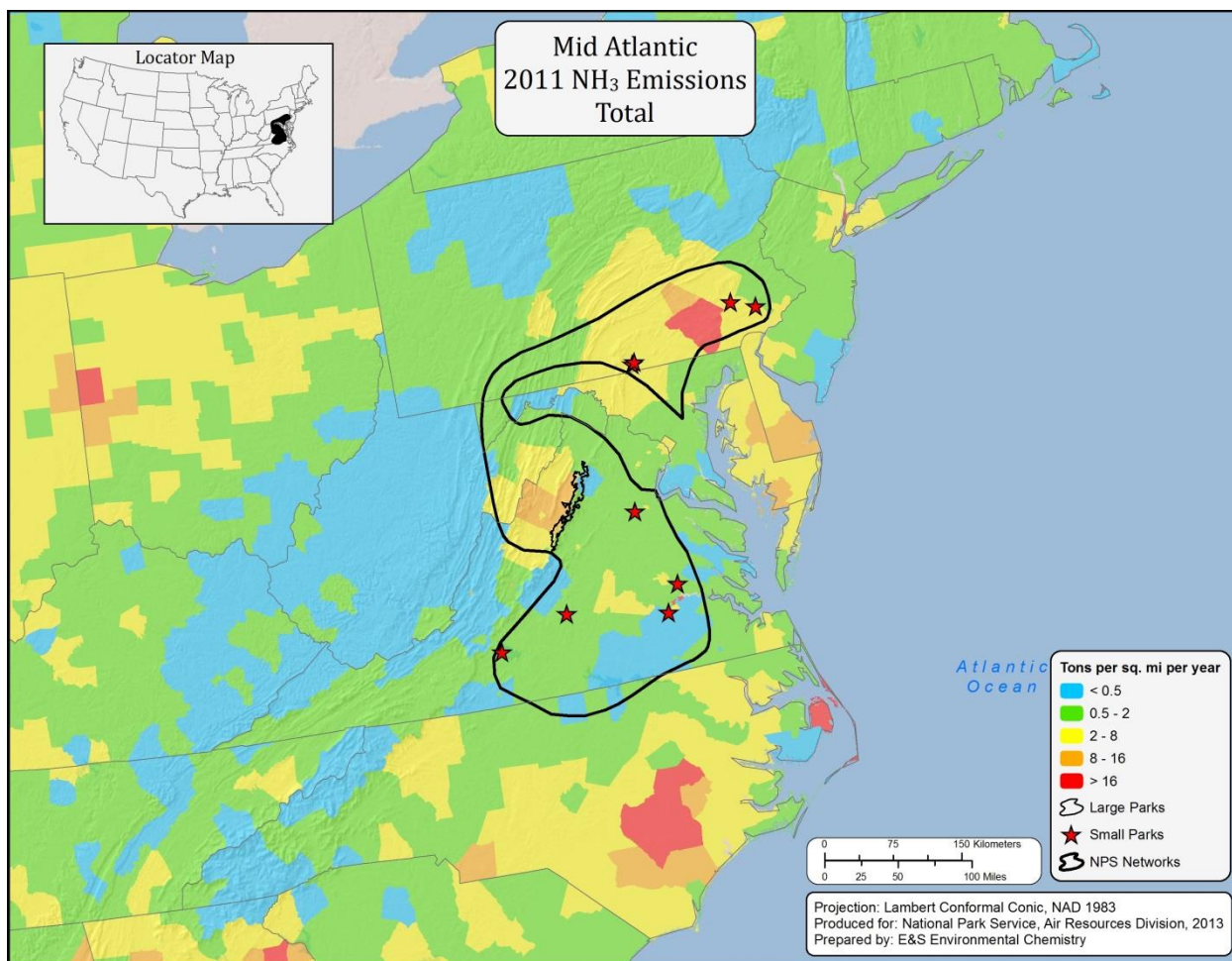
Recently, Schwede and Lear (2014) documented a hybrid approach developed by the National Atmospheric Deposition Program (NADP) Total Deposition (TDEP) Science Committee for estimating total N and S deposition. This approach combined monitoring and modeling data. Modeling was accomplished using the Community Multiscale Air Quality (CMAQ) model (Byun and Schere 2006). Priority was given to measured data near the locations of the monitors and to modeled data where monitoring data were not available. In addition, CMAQ data were used for N species that are not routinely measured in the monitoring programs: peroxyacetyl nitrate (PAN), N₂O₅, NO, NO₂, HONO, and organic NO₃. The total deposition estimates are considered to be dynamic, with updates planned as new information becomes available. TDEP data reported here were developed in late 2013 and are designated version 2013.02.



Map 2. Total SO₂ emissions, by county, near MIDN for the year 2011. Data from EPA's National Emissions Inventory.



Map 3. Total NO_x emissions, by county, near MIDN for the year 2011. Data from EPA's National Emissions Inventory.



Map 4. Total NH₃ emissions, by county, near MIDN for the year 2011. Data from EPA's National Emissions Inventory.

Atmospheric S, and to a lesser extent N, deposition levels have declined at all MIDN parks since 2001, based on TDEP estimates (Table 1). Decreases in total S deposition over the previous decade for the parks in this network ranged from 26.4% at BOWA to 52.5% at APCO. Estimated total N deposition decreased over that same time period in MIDN parks by varying amounts. Oxidized and reduced N showed opposite patterns, with oxidized N decreasing and reduced N increasing at almost all of the parks in the network since the monitoring period 2000-2002.

Total S deposition in and around MIDN for the period 2010-2012 was generally highest (> 10 kg S/ha/yr) to the north and lowest (< 5 kg S/ha/yr) to the south within the network area (Map 5). Oxidized inorganic N deposition for the period 2010-2012 was in the range of 2 to 5 kg N/ha/yr at the park lands to the southwest within MIDN and 5 to 10 kg N/ha/yr in the eastern portion of the network (Map 6). Most areas to the south received less than 5 kg N/ha/yr of reduced inorganic N from atmospheric deposition during this same period (Map 7); parks to the northeast received higher (> 5 kg N/ha/yr) amounts. Total N deposition was more than 5 kg N/ha/yr at most park locations in the MIDN (Map 8); some park lands received higher amounts, more than 15 kg N/ha/yr.

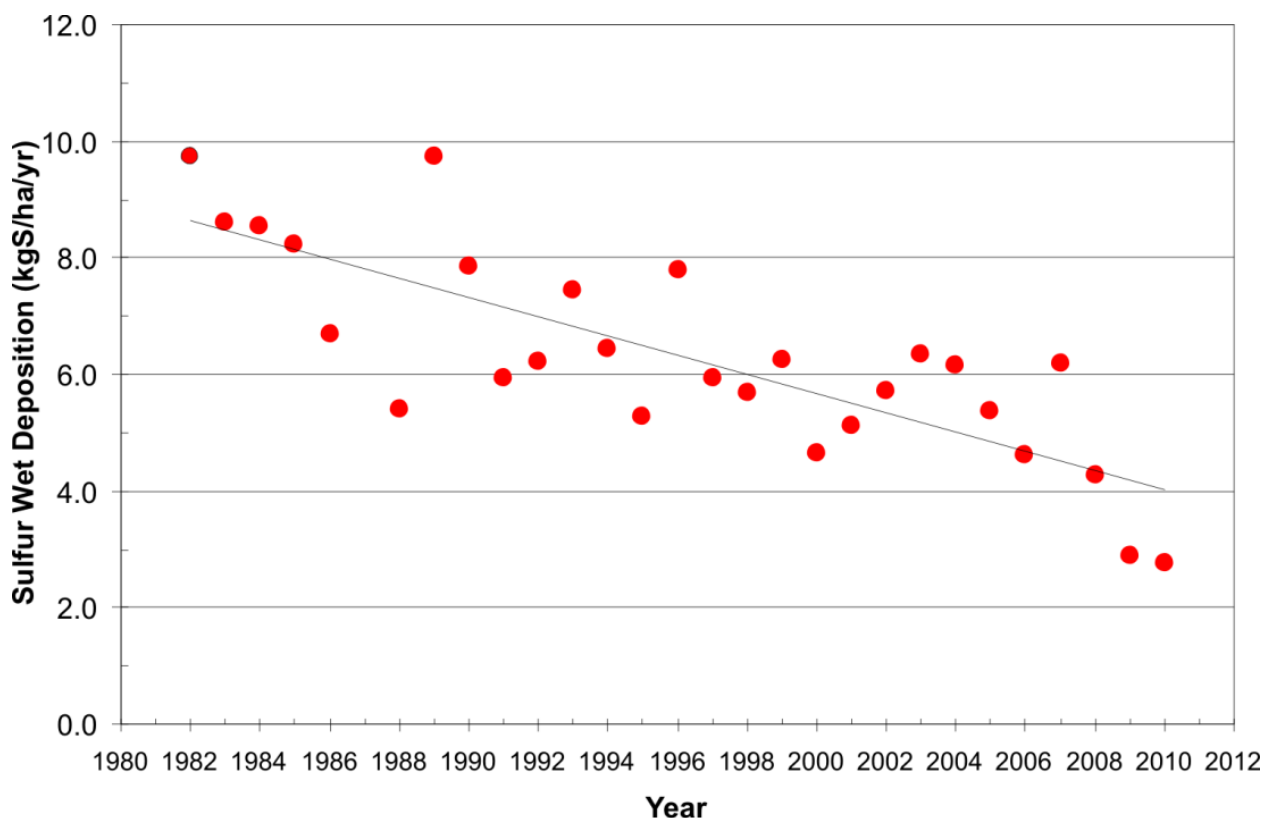


Figure 1. This graph shows wet sulfur deposition for the period of record at the Big Meadows monitoring station in Shenandoah National Park. Total sulfur deposition, including both wet and dry forms, is probably at least one and a half times these measured wet-only values. Sulfur deposition in the park has decreased by more than 50% over the past three decades in response to emissions control legislation.

Wet deposition collected at 29 national park locations was reported by NPS (2010). Most monitored sites showed statistically significant ($p \leq 0.05$) decreases in concentrations of sulfate (SO_4^{2-}) in wet deposition between about 1989 and about 2008. One of the largest decreasing trends was reported for SHEN ($-0.77 \mu\text{eq/L/yr}$; NPS 2010), second only to Indiana Dunes in the Great Lakes Network ($-1.4 \mu\text{eq/L/yr}$). There was not, however, a statistically significant change in nitrate (NO_3^-) concentration in wet deposition at SHEN during that period. Concentrations of NO_3^- in wet deposition during the period 1989 to 2008 decreased by statistically significant ($p \leq 0.05$) amounts at four locations and increased by a statistically significant amount at one park. Wet NO_3^- deposition was unchanged at the other 24 monitored park locations, including SHEN.

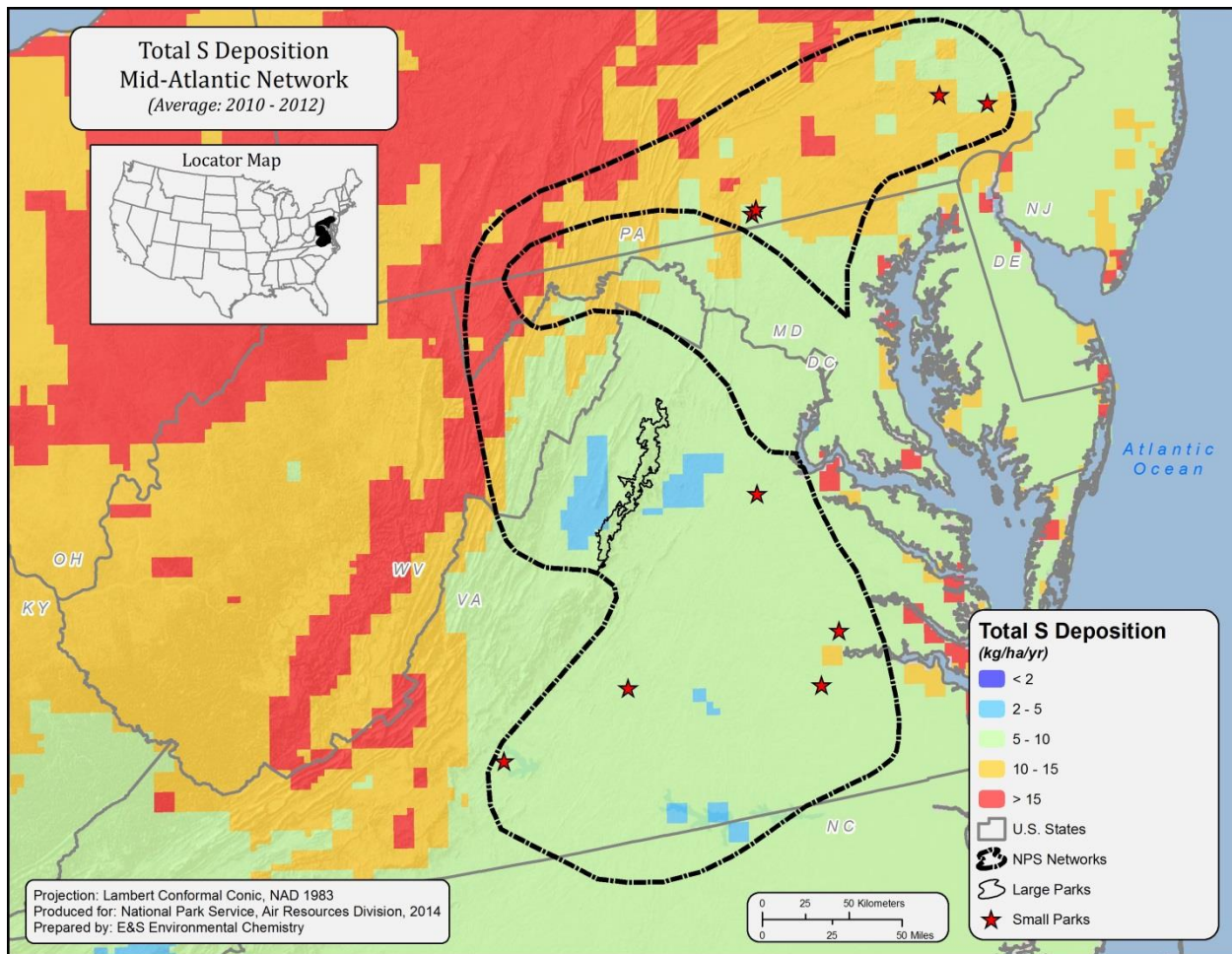
NPS (2010) also reported long-term trends in concentrations of Hg in wet deposition in SHEN and eight other national parks during the period 2003 through 2008. Statistically significant ($p \leq 0.05$) decreases in wet Hg deposition were reported for two parks, but Hg deposition remained unchanged at SHEN. Three-year means of annual Hg concentration in wet deposition were reported by NPS (2010) for 13 parks that had at least two years of valid data during the period 2006-2008. SHEN was among the five monitored parks having highest Hg concentrations in precipitation.

Table 1. Average changes in S and N deposition between 2001 and 2011 across park grid cells at MIDN parks. Deposition estimates were determined by the Total Deposition Project, TDEP, based on three-year averages centered on 2001 and 2011 for all ~4 km grid cells in each park. The minimum, maximum, and range of 2011 S and N deposition within each park are also shown.

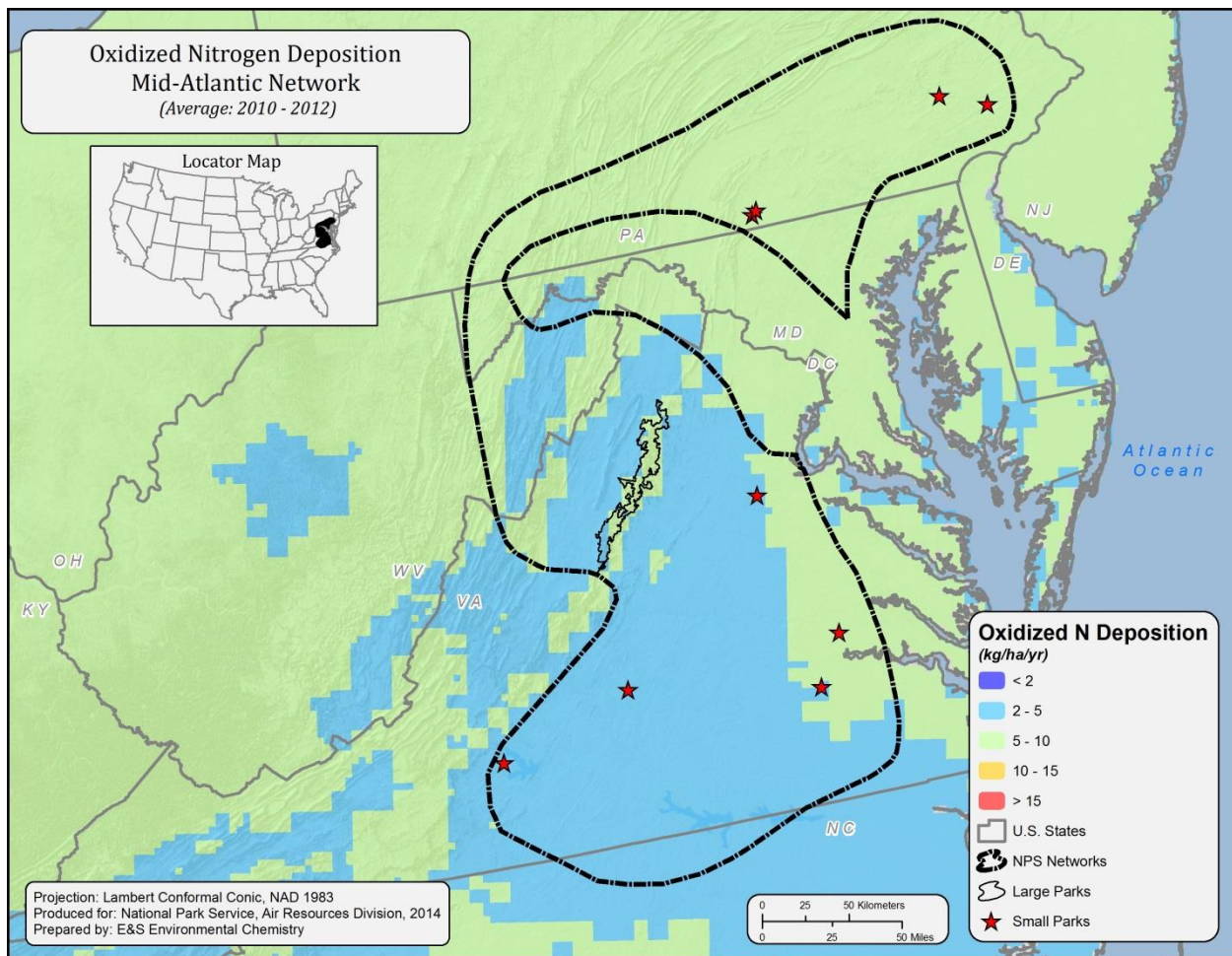
Park Code	Park Name	Parameter	2001 Average (kg/ha/yr)	2011 Average (kg/ha/yr)	Absolute Change (kg/ha/yr)	Percent Change	2011 Minimum (kg/ha/yr)	2011 Maximum (kg/ha/yr)	2011 Range (kg/ha/yr)
APCO	Appomattox Court House	Total S	11.39	5.41	-5.98	-52.5%	5.39	5.41	0.01
		Total N	10.87	7.90	-2.97	-27.3%	7.90	7.91	0.01
		Oxidized N	7.96	4.70	-3.27	-41.0%	4.69	4.71	0.02
		Reduced N	2.91	3.20	0.30	10.3%	3.20	3.20	0.01
BOWA	Booker T. Washington	Total S	11.07	8.15	-2.92	-26.4%	8.15	8.15	0.00
		Total N	9.54	7.74	-1.80	-18.9%	7.74	7.74	0.00
		Oxidized N	6.95	4.67	-2.27	-32.7%	4.67	4.67	0.00
		Reduced N	2.60	3.07	0.47	18.1%	3.07	3.07	0.00
EISE	Eisenhower	Total S	19.85	9.79	-10.06	-50.7%	9.79	9.94	0.16
		Total N	18.30	15.67	-2.63	-14.4%	15.66	15.94	0.29
		Oxidized N	11.05	6.49	-4.56	-41.2%	6.49	6.60	0.12
		Reduced N	7.25	9.18	1.93	26.6%	9.17	9.34	0.17
FRSP	Fredericksburg and Spotsylvania	Total S	12.69	6.20	-6.49	-51.2%	5.63	6.97	1.33
		Total N	11.83	8.13	-3.70	-31.3%	7.98	8.72	0.74
		Oxidized N	8.85	4.85	-4.00	-45.2%	4.45	5.56	1.10
		Reduced N	2.98	3.28	0.31	10.3%	3.08	3.59	0.51
GETT	Gettysburg	Total S	19.77	9.84	-9.93	-50.2%	9.35	10.05	0.70
		Total N	18.26	15.78	-2.48	-13.6%	15.06	16.13	1.07
		Oxidized N	11.02	6.53	-4.49	-40.7%	6.23	6.67	0.44
		Reduced N	7.23	9.24	2.01	27.8%	8.82	9.45	0.63

Table 1 (continued). Average changes in S and N deposition between 2001 and 2011 across park grid cells at MIDN parks. Deposition estimates were determined by the U.S. EPA's Total Deposition Project, TDEP, based on three-year averages centered on 2001 and 2011 for all ~4 km grid cells in each park. The minimum, maximum, and range of 2011 S and N deposition within each park are also shown.

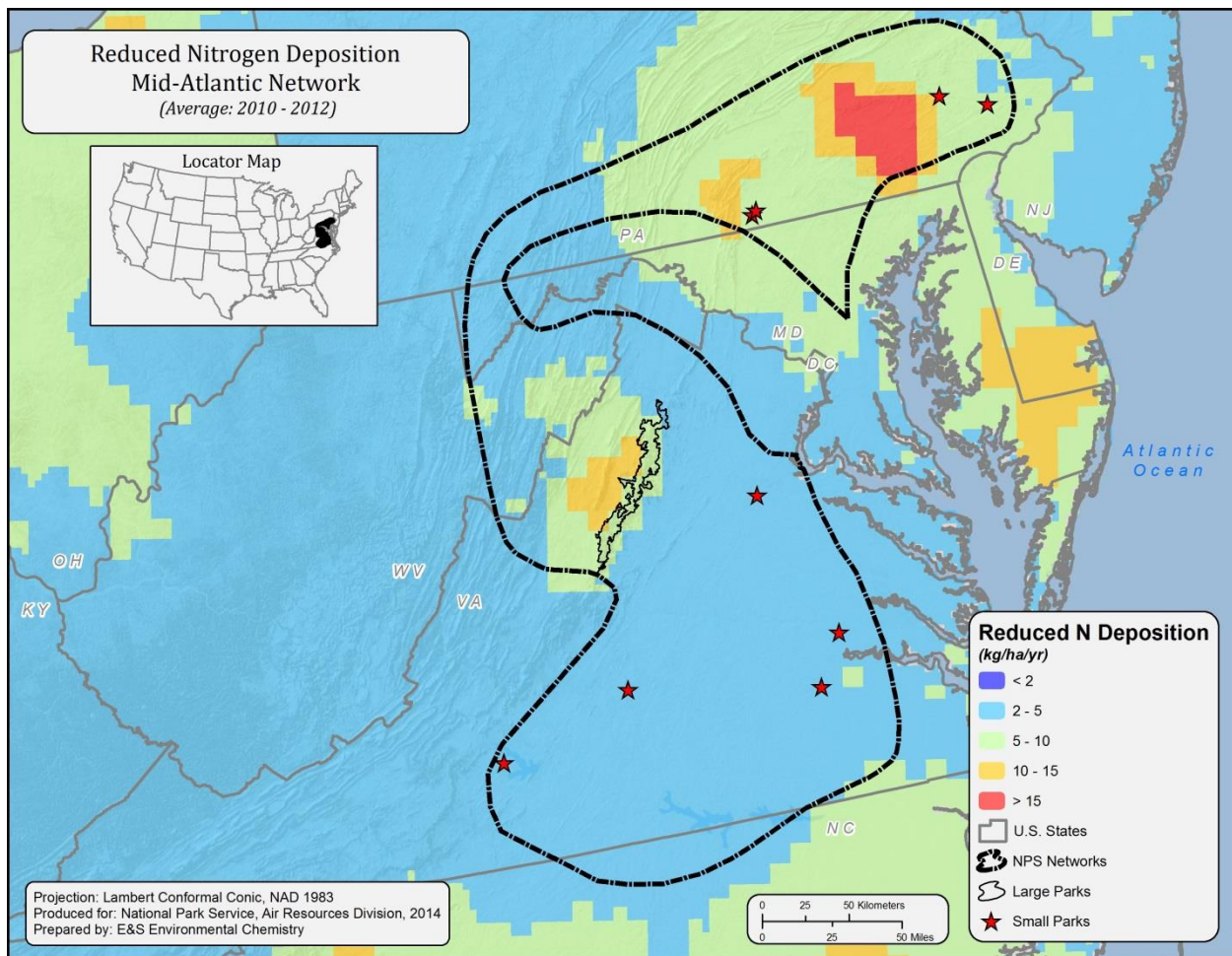
Park Code	Park Name	Parameter	2001 Average (kg/ha/yr)	2011 Average (kg/ha/yr)	Absolute Change (kg/ha/yr)	Percent Change	2011 Minimum (kg/ha/yr)	2011 Maximum (kg/ha/yr)	2011 Range (kg/ha/yr)
HOFU	Hopewell Furnace	Total S	17.70	10.21	-7.50	-42.3%	10.14	10.41	0.27
		Total N	17.94	15.13	-2.81	-15.7%	13.88	15.52	1.64
		Oxidized N	12.04	7.56	-4.48	-37.2%	7.16	7.68	0.52
		Reduced N	5.90	7.58	1.67	28.3%	6.72	7.84	1.12
PETE	Petersburg	Total S	12.62	7.40	-5.22	-41.5%	5.93	9.66	3.74
		Total N	14.00	8.94	-5.05	-36.0%	8.46	10.51	2.04
		Oxidized N	8.91	5.19	-3.72	-41.7%	4.84	5.97	1.13
		Reduced N	5.08	3.75	-1.33	-25.9%	3.63	4.54	0.91
RICH	Richmond	Total S	14.04	8.57	-5.47	-38.8%	6.98	13.43	6.45
		Total N	12.59	9.46	-3.13	-24.3%	8.76	9.75	1.00
		Oxidized N	9.30	6.01	-3.30	-35.0%	5.50	6.15	0.65
		Reduced N	3.28	3.45	0.17	6.1%	3.25	3.94	0.69
SHEN	Shenandoah	Total S	13.05	6.98	-6.08	-46.7%	4.52	8.02	3.49
		Total N	13.60	12.75	-0.85	-6.2%	8.74	16.95	8.21
		Oxidized N	8.42	5.23	-3.20	-38.0%	3.45	5.95	2.50
		Reduced N	5.18	7.51	2.35	48.1%	3.88	12.99	9.11
VAFO	Valley Forge	Total S	17.56	9.95	-7.61	-43.3%	9.92	9.96	0.05
		Total N	17.69	14.35	-3.34	-18.9%	14.33	14.38	0.06
		Oxidized N	12.91	8.45	-4.47	-34.6%	8.42	8.45	0.03
		Reduced N	4.77	5.90	1.13	23.6%	5.90	5.93	0.04



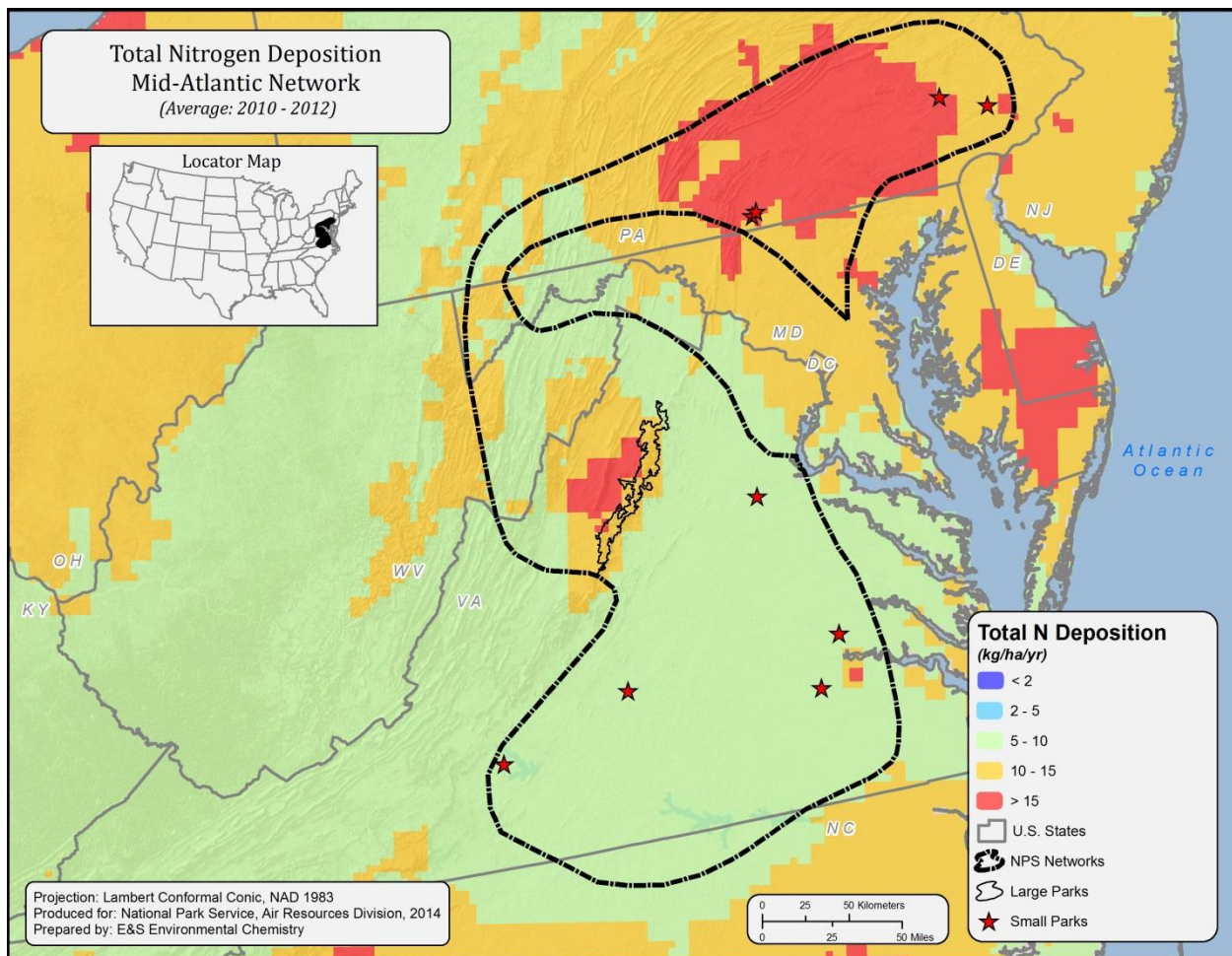
Map 5. Total S deposition for the three-year period centered on 2011 in and around MIDN. (Source: Schwede and Lear 2014)



Map 6. Total oxidized inorganic N deposition for the three-year period centered on 2011 in and around MIDN. (Source: Schwede and Lear 2014)



Map 7. Reduced inorganic N deposition for the three-year period centered on 2011 in and around MIDN. (Source: Schwede and Lear 2014)



Map 8. Total N deposition for the three-year period centered on 2011 in and around MIDN. (Source: Schwede and Lear 2014)

Acidification

The network rankings developed by Sullivan et al. (2011b) in a coarse screening assessment for acid Pollutant Exposure, Ecosystem Sensitivity to acidification, and Park Protection yielded an overall network acidification Summary Risk ranking for the MIDN that was the highest among all networks. The overall level of concern for acidification effects on Inventory and Monitoring (I&M) Program parks within this network was judged by Sullivan et al. (2011b) to be Very High.

SHEN was ranked Very High (Table 2) among parks by Sullivan et al. (2011b) in both acid Pollutant Exposure and Ecosystem Sensitivity to acidification, near the top among all I&M parks. This was due to both the presence of nearby pollution sources and substantial acid-sensitive resources in SHEN. All of the smaller historical parks in this network were ranked Very High or High in acid Pollutant Exposure (Table 2). The smaller parks were variable in their rankings for Ecosystem Sensitivity to acidification, from Very Low in BOWA to Moderate in VAFO, HOFU, and GETT (Table 2). None of the smaller parks are expected to be as sensitive to acidic deposition as SHEN because SHEN is the only MIDN park located along the ridgeline of the Appalachian Mountains. While rankings are an indication of risk, park-specific data, particularly data on ecosystem sensitivity, are needed to fully evaluate risk from acidification.

Ecosystem sensitivity to acidification rankings reported by Sullivan et al. (2011b) take into account elevation and land slope, which often influence the degree of acid neutralization provided by soils and bedrock within the watershed. Land slope tends to be fairly steep in SHEN because of its location along the ridgeline of the Appalachian Mountains. The entire park has average slope in the 30° to 40° range, suggesting increased potential for acid sensitivity of aquatic ecosystems. All other parks within the MIDN are much less steep, with average slope less than 10° in all but one park (HOFU), which has average slope in the 10° to 20° range (Sullivan et al. 2011b).

Table 2. Estimated I&M park rankings¹ according to risk of acidification impacts on sensitive receptors (Source: Sullivan et al. 2011b)

Park Name ²	Park Code	Estimated Acid Pollutant Exposure	Estimated Ecosystem Sensitivity to Acidification
Appomattox Court House	APCO	High	Low
Booker T. Washington	BOWA	High	Very Low
Eisenhower	EISE	Very High	Low
Fredericksburg and Spotsylvania	FRSP	Very High	Low
Gettysburg	GETT	Very High	Moderate
Hopewell Furnace	HOFU	Very High	Moderate
Petersburg	PETE	Very High	Low
Richmond	RICH	Very High	Low
<i>Shenandoah</i>	SHEN	Very High	Very High
Valley Forge	VAFO	Very High	Moderate

¹ Relative park rankings are designated according to quintile ranking, among all I&M Parks, from the lowest quintile (Very Low risk) to the highest quintile (Very High risk).

² Park names are printed in bold italic for parks larger than 100 mi².

Sulfur deposition has been high enough at SHEN to cause the acidification of many streams within the park, with associated harmful impacts to fish, aquatic insects, and other life forms. Nitrogen deposition has also been relatively high but, because deposited N has been strongly retained in soils and vegetation, it has constituted only a minor contributor to stream acidification to date.

Sulfate mass balance analyses indicated that, because of watershed S retention, soils and surface waters of the MIDN and southward throughout the southern Appalachian Mountain region have not yet realized the full effects of elevated S deposition. On average, based on National Stream Survey (NSS) data, sites in the Blue Ridge Mountains retained 35% of incoming S from atmospheric deposition. Herlihy et al. (1996) concluded that S retention will likely continue to decrease in the future, resulting in further losses of stream ANC.

Sulfur-adsorption varies by physiographic province in the Appalachian Mountain region. It is highest in the soils of the southern Blue Ridge, where typically about half of the incoming S is retained. Adsorption is lower in the Valley and Ridge watersheds to the west of SHEN and especially in the Appalachian Plateau (Herlihy et al. 1993). In general, S adsorption is moderate in the vicinity of SHEN and higher in the southern portions of the Blue Ridge Province.

Acidification of Terrestrial Ecosystems

Available evidence regarding the effects of acidic deposition on terrestrial resources in the southern Appalachian Mountains was reviewed by Eagar et al. (1996) and Sullivan et al. (2002). Possible mechanisms for acidification impacts on terrestrial ecosystems include soil acidification, increased concentration of aluminum (Al) in soil solution, and decreased availability of base cations. These mechanisms are inter-related. Some acid-sensitive forest soils have been acidified by S and N deposition. Effects have been most pronounced at high elevation in areas occupied by coniferous and northern hardwood forests, and have included reduced exchangeable calcium (Ca^{2+}) and soil base saturation (BS), and decreased Ca:Al ratio in soil solution. Decreases in concentrations of exchangeable base cations, a known effect of acidic deposition, in the Oa and B soil horizons over the past several decades are common in the eastern United States. To some degree, soils can recover their base cation reserves over time in response to reduced future levels of acidic deposition. However, the recovery potential of soil exchangeable base cation concentrations is dependent on weathering rates, which are slow and uncertain.

In 2000, University of Virginia scientists collected and analyzed soil samples at 79 sites within SHEN in support of the acidic deposition component of the Sullivan et al. (2003) assessment. The samples were collected from 14 different watersheds, 5 each on primarily siliciclastic and basaltic bedrock and 4 primarily on granitic bedrock. Between four and eight soil pits were excavated within each watershed, distributed across each watershed to account for differences in slope, aspect, land use history, fire history, and forest cover type. Laboratory analyses were conducted by Pennsylvania State University and Virginia Polytechnic Institute and State University (Welsch et al. 2001).

The soils within watersheds situated primarily on siliciclastic bedrock generally showed the lowest soil pH (median 4.4 to 4.5), cation exchange capacity (CEC; median 3.5 to 7.5 cmol/kg), and BS (median 8 to 12%). Values for watersheds having soils primarily on granitic bedrock were generally

intermediate (BS less than about 14%), and basaltic watersheds were higher in all three parameters (Table 3). The range of BS values obtained for soils associated with both siliciclastic and granitic bedrock in SHEN (Welsch et al. 2001) included values in the 10% to 20% range cited as possible threshold values for incomplete acid neutralization and leaching of Al (Binkley et al. 1989, Cronan and Schofield 1990, Reuss and Johnson 1986). Also, the measured pH of soils located over both siliciclastic and granitic bedrock included values in the highly acidic range (pH < 4.5) in which the more toxic forms of Al often predominate (Binkley et al. 1989). The low base cation availability in soils of watersheds underlain by siliciclastic or granitic bedrock was probably due to a combination of low base cation content of the parent bedrock and depletion by previous land use and decades of accelerated leaching by acidic deposition. The relative importance of these factors is not known. This low base cation availability suggests the potential for leaching of Al to streams. It is not clear whether forest soils at SHEN will ultimately develop Ca²⁺ deficiency. Soils may stop changing their base cation status before deficiencies develop as acidic deposition levels decline, or weathering rates may be sufficient to maintain adequate cation nutrient supplies.

Table 3. Interquartile distribution of pH, cation exchange capacity (CEC), and percent base saturation for soil samples¹ collected in SHEN study watersheds during the 2000 soil survey. (Source: Sullivan et al. 2003)

Site ID	Watershed	n	pH			CEC (cmol/kg)			Percent Base Saturation		
			25th	Med	75th	25th	Med	75th	25th	Med	75th
Siliciclastic Bedrock Class ²											
VT35	Paine Run	6	4.4	4.5	4.7	3.7	5.7	5.7	7.1	10.0	24.9
WOR1	White Oak Run	6	4.3	4.4	4.4	4.8	7.5	7.8	5.3	7.5	8.5
DR01	Deep Run	5	4.3	4.4	4.5	3.9	5.0	5.8	7.2	8.9	10.8
VT36	Meadow Run	6	4.4	4.4	4.5	3.1	3.5	7.6	7.8	8.7	11.3
VT53	Twomile Run	5	4.3	4.5	4.5	4.6	6.0	6.9	11.7	12.3	13.6
Granitic Bedrock Class											
VT59	Staunton River	6	4.7	4.8	4.9	6.5	7.5	9.2	9.1	13.9	29.5
NFDR	NF of Dry Run	5	4.4	4.5	4.7	7.3	8.0	9.2	7.5	10.8	12.4
VT58	Brokenback Run	5	4.6	4.7	4.7	7.3	8.4	9.6	6.0	6.7	9.7
VT62	Hazel River	4	4.5	4.7	4.8	5.3	5.3	6.5	12.3	12.8	21.6
Basaltic Bedrock Class											
VT60	Piney River	6	4.7	5.0	5.3	7.3	7.7	10.0	17.0	24.0	57.0
VT66	Rose River	8	4.8	5.0	5.3	7.3	10.1	10.7	19.1	38.0	63.5
VT75	White Oak Canyon	6	4.9	5.1	5.5	7.1	7.5	9.3	15.6	32.8	43.4
VT61	NF of Thornton River	7	5.1	5.2	5.3	7.7	9.6	10.8	35.6	54.4	71.2
VT51	Jeremys Run	4	4.7	5.0	5.3	6.3	7.6	7.7	15.0	22.8	46.1

¹ Samples collected from mineral soil >20cm depth

² Watersheds are stratified according to the predominant bedrock class present in each watershed.

Soil acidification, Al toxicity, and exposure of foliage to acidic deposition have collectively contributed to decline in red spruce (*Picea rubens*), sugar maple (*Acer saccharum*), and perhaps

other tree species in portions of the northeastern United States and Appalachian Mountains, likely including within SHEN, that have experienced soil acidification as a consequence of oxidized sulfur (SO_x) and NO_x deposition. Effects have included reduced growth and increased stress to overstory trees, and likely changes in the species distributions of understory plants. Nearly all of SHEN is covered by vegetation types likely to contain sugar maple. Sugar maple is known to be sensitive to acidification from atmospheric S and N input. Deposition of both S and N are of concern with respect to potential acidification effects on forest vegetation throughout the Appalachian Mountains, including within SHEN, but probably not at the other MIDN parks. Potentially sensitive spruce-fir forest resources are found at high elevation (generally above about 1,370 m) in the southern Appalachian Mountains. There are small (~18 ha) relic populations of red spruce in SHEN at Limberlost and Hawksbill Peak (NPS 1981). These populations are likely under considerable natural stress and may be more susceptible to the effects of high S and/or N deposition than other forest types in SHEN.

There is no clear evidence to demonstrate that the levels of N deposition observed in SHEN have caused forest decline in the deciduous forests of the park. The highest point in the park is only 1,234 m, which is below the elevation at which cloud deposition of S and N has been shown to be a large contributor to total S and N deposition. Sigmon et al. (1989) estimated total warm season cloud deposition at the Pinnacles of SHEN (1,014 m elevation) equal to 0.9, 0.7, and 0.2 kg/ha/mo, respectively, for SO_4^{2-} , NO_3^- , and ammonium (NH_4^+). These cloud deposition estimates contrast with the estimates by Lindberg et al. (1988) at Great Smoky Mountains National Park (GRSM; 1,740 m elevation) that were more than three-fold higher for NO_3^- , eight-fold higher for SO_4^{2-} , and five-fold higher for NH_4^+ (c.f., Vong et al. 1991). Due to high cloud deposition, total S and N deposition levels are therefore much higher at GRSM than at SHEN. Because the forests in SHEN are almost exclusively second growth, subsequent to large-scale timber harvesting and localized agricultural land use prior to park creation, the N-demand of the regrowing forest is likely to be high. This precludes NO_3^- leaching at current N deposition levels in the absence of significant disturbance such as was seen with gypsy moth (*Lymantria dispar*) infestation. It is not known to what extent recent loss of eastern hemlock (*Tsuga canadensis*) trees in portions of the park might affect N leaching.

Nevertheless, the complex relationships between atmospheric inputs and forest health remain a concern in SHEN, especially in view of the known effects of acidic deposition on soil acidity, nutrient supply, metal toxicity, and tree growth. It is not known whether forest ecosystems at SHEN are currently experiencing subtle effects of elevated N deposition, and whether, for example, some plant species are favored at the expense of other species by the relatively high N environment.

Effects of insect-caused defoliation on the N cycle can be pronounced. The foliar N consumed by insects is deposited on the forest floor as insect feces (frass), greenfall, and insect biomass. Some of this deposited N is subsequently taken up by tree roots and soil microbes, with little effect on the nutritional condition of the trees or the site. Where a sizable component of this N is leached in drainage water, the nutritional consequences can be more significant. There are also various feedback mechanisms. For example, low N supply can slow the population growth of defoliating insects (Mason et al. 1992) and enhance the tree's chemical defenses against insects (Hunter and Schultz

1995). The amount of N leaching loss is generally small, relative to atmospheric deposition inputs and relative to the amount of N transferred to the forest floor with the defoliation (Lovett and Ruesink 1995, Lovett et al. 2002). Nevertheless, it can be high enough to contribute to base cation depletion of soils and effects on downstream receiving waters. The extent of NO_3^- leaching may be partly related to the extent of defoliation and tree mortality that occurs and also to the amount of precipitation that occurs immediately after the defoliation (Lovett et al. 2002).

With respect to the risk factors generally associated with acidification effects on forest vegetation in some other areas of the southern Appalachian Mountains, it appears that forests in SHEN may be relatively less susceptible to harm. Nonetheless, examination of the available soils information for SHEN watersheds suggests that there may be some risk of adverse effects and that the degree of risk varies spatially within the park.

The sensitivity of forest soils to acidification in MIDN parks other than SHEN is less well known. However, forest vegetation condition monitoring in MIDN parks began in 2007 (Comiskey et al. 2009, Comiskey 2013). This monitoring program is intended to provide a framework for tracking long-term change across the forests in the MIDN parks. A network of vegetation plots has been installed in eight of the MIDN parks (APCO, BOWA, FRSP, GETT, HOFU, PETE, RICH, and VAFO). SHEN uses a different protocol (Cass et al. 2011); EISE has low forest cover and is not monitored. This monitoring effort focuses on forest structure, composition, and the dynamics of canopy and understory woody plant species. Part of the effort is also focused on the status and trends in soil Ca:Al ratio as a relative index of base cation depletion and increased Al availability in MIDN forest soils. A ratio of soil Ca:Al higher than 4 is interpreted as indicating relatively good Ca availability. The median observed Ca:Al in 2012 in the surveyed parks considered here was rated as good only in APCO, BOWA, and GETT. Ratios were lowest (less than 1.0) in FRSP and PETE.

Acidification of Aquatic Ecosystems

Acidic streams and streams with very low ANC in the MIDN are almost all located in small (watershed area < 20 km²), upland, forested catchments in areas of base-poor bedrock. Thin soils and steep slopes make these watersheds unsuitable for agriculture and other development and contribute to their sensitivity to acidic deposition (Baker et al. 1990c).

In the subpopulation of upland forested streams, which comprises about half of the total stream population in the mid-Appalachian area, data from various local surveys showed that 5% to 20% of the streams were acidic, and about 25% to 50% had ANC < 50 $\mu\text{eq/L}$ (Herlihy et al. 1993). NSS estimates for the whole region showed that there were 2,330 km of acidic streams and 7,500 km of streams with ANC < 50 $\mu\text{eq/L}$. In the forested reaches, 12% of the upstream reaches were acidic and 17% had pH $\leq$ 5.5. Sulfur is the primary determinant of precipitation acidity and SO_4^{2-} is the dominant acid anion associated with acidic streams, both in the central Appalachian Mountains region and within SHEN. Sulfur deposition has acidified park streams and affected in-stream biota, particularly in watersheds dominated by siliciclastic bedrock types that give rise to soils with low base saturation and relatively low sulfur adsorption, and to streams with low ANC. Nitrate concentrations in SHEN streams are negligible in the absence of insect infestation.

There are no high-elevation lakes in SHEN, but there is considerable length of high-elevation streams. Higher-elevation streams are generally considered potentially more susceptible to acidification from atmospheric S and N input than lower-elevation streams. All streams in the park are first or second-order.

Aquatic effects research at SHEN has contributed significantly to the development of scientific understanding of watershed processes that control aquatic effects of acidic deposition (c.f., Galloway et al. 1983). This research has also contributed to understanding of relationships between geology and sensitivity to acidification (Bricker and Rice 1989, Lynch and Dise 1985, Sullivan et al. 2007) and of the effects of forest insect infestation on episodic chemical processes (Eshleman et al. 2001, Webb et al. 1995).

Streamwater ANC is closely related to bedrock mineralogy in the MIDN and surrounding areas (Herlihy et al. 1993). In fact, geological type, soils conditions that developed from underlying geology, and water chemistry conditions are all closely interrelated within the network. This is partly because rock and soils materials in the MIDN and elsewhere in the Southeast were not transported from place to place (and thereby mixed) by the process of glaciation. Sullivan et al. (2007) delimited a high-interest area for streamwater acidification sensitivity within the southern Appalachian Mountain region (Virginia/West Virginia to Georgia) based on geological classification and elevation. It covered only 28% of the region, and yet included almost all known acidic and low ANC ($< 20 \mu\text{eq/L}$) streams, based on evaluation of about 1,000 streams for which water chemistry data were available. They found that the vast majority of low-ANC sampled streams were underlain by the siliceous geologic sensitivity class, which is represented by such lithologies as sandstone and quartzite. Low-ANC streamwater throughout the region was also found to be associated with a number of watershed features in addition to lithology and elevation, including ecoregion, physiographic province, soil type, forest type and watershed area. More recent data on regional stream chemistry (including beyond the boundaries of SHEN) can be found at <http://people.virginia.edu/~swas/POST/scripts/overview.php>.

The SHEN landscape includes three major geologic sensitivity types: siliciclastic, granitic, and basaltic. Each of these bedrock types influences about one-third of the stream length in the park. The observed patterns in streamwater chemistry in SHEN are strongly related to patterns in bedrock geology (Sullivan et al. 2003). As observed by Sullivan et al. (2007) elsewhere in the region, siliciclastic sites have the greatest sensitivity to acidification, whereas granitic sites have moderate sensitivity and basaltic sites have low sensitivity. There are many streams on siliciclastic bedrock in SHEN that have chronic ANC in the range where adverse effects are likely to occur on sensitive aquatic biota and where episodic acidification to ANC values near or below zero frequently occur during hydrological events. The streams that are most susceptible to adverse chronic or episodic effects on in-stream biota are those having chronic ANC less than about $50 \mu\text{eq/L}$, especially those having chronic ANC less than about $20 \mu\text{eq/L}$. These are primarily situated on siliciclastic bedrock.

The Shenandoah Watershed Study (SWAS) was initiated in 1979, with the establishment of water quality monitoring on two streams (Webb et al. 1993). The current watershed data collection involves 14 primary study watersheds, including a combination of discharge gauging, routine

quarterly and weekly water quality sampling, and high-frequency episodic, or storm-flow, sampling (Cosby et al. 2006, Galloway et al. 1999). In addition, a number of extensive stream chemistry surveys, fish population surveys, and other watershed data collection efforts have been conducted throughout the park in support of various research efforts. The SWAS program is coordinated with the Virginia Trout Stream Sensitivity Study (VTSSS), which extends quarterly sampling to an additional 51 native brook trout (*Salvelinus fontinalis*) streams located on public lands throughout western Virginia (primarily in the George Washington and Jefferson National Forests).

Since the 1980s, the SWAS program has developed a uniquely comprehensive watershed database for SHEN, while making major contributions to scientific understanding of surface water acidification and the biogeochemistry of forested mountain watersheds. Data and analyses provided through SWAS have contributed significantly to regional and national assessments of acidic deposition effects, including several that led to enactment of the Clean Air Act Amendments (CAAA) of 1990 (e.g., Baker et al. 1990a, National Acid Precipitation Assessment Program (NAPAP) 1991). The SWAS and VTSSS programs have provided some of the most comprehensive data available for use in aquatic effects assessment such as conducted as part of the Southern Appalachian Mountain Initiative (SAMI), a multistate, multiagency effort to address the air pollution problem in the southern Appalachian region (Sullivan et al. 2002). The combined SWAS and VTSSS programs contributed data to the U.S. Environmental Protection Agency (EPA) for use in Congressionally mandated evaluation of air pollution control program benefits relative to acidic deposition effects on sensitive surface waters. As a consequence of this extensive monitoring, research, and assessment activity, SHEN is a leader among the national parks with respect to park-specific knowledge of acidic deposition effects and watershed ecosystem conditions in general.

All of the primary SWAS streams on siliciclastic bedrock that were monitored during the period 1988 to 1999 had relatively high median SO_4^{2-} concentration (76 to 109 $\mu\text{eq/L}$), whereas three of four streams monitored on granitic bedrock had SO_4^{2-} concentration $< 43 \mu\text{eq/L}$ (Webb et al. 2004). Sulfate concentrations in streams draining basaltic bedrock were more variable, ranging from 52 to 127 $\mu\text{eq/L}$. Streamwater base cation concentrations and ANC also varied dramatically from site to site. Median streamwater base cation concentrations were generally lowest in the watersheds on siliciclastic bedrock, and this could reflect lower base cation supply from watershed soils and/or greater base cation depletion of soils caused by leaching of SO_4^{2-} to streams. Base cation concentrations were substantially higher (median $> 235 \mu\text{eq/L}$) in watersheds on basaltic bedrock.

A clear relationship was found between streamwater ANC and measured soil base saturation among the SWAS watersheds (Figure 2). All watersheds that were characterized by soil base saturation less than 15% had average streamwater ANC $< 100 \mu\text{eq/L}$. Watersheds that had higher soil base saturation (all of which were $> 22\%$) were dominated by the basaltic bedrock type and had average streamwater ANC $> 100 \mu\text{eq/L}$. Lowest base saturation values (7% to 14%) were found in the siliciclastic and granitic watersheds, with much higher values in the basaltic watersheds.

Although N is thought to play an important role in the chronic acidification of streams in some areas (cf., Sullivan et al. 1997), N is generally tightly cycled in SHEN and does not usually contribute significantly to streamwater acidification. However, forest insect infestations can provide a dramatic

exception: the gypsy moth infestation traversed SHEN and affected all of the SWAS study watersheds (Webb 1999). The repeated consumption and processing of foliage by the gypsy moth larvae disrupted the ordinarily tight cycling of N in SHEN forests. Some areas of the park were heavily defoliated 2 to 3 years in a row. The White Oak Run watershed, for example, was more than 90% defoliated in both 1991 and 1992. This insect infestation of forest ecosystems in SHEN resulted in substantial effects on streamwater chemistry. The most notable effects of the defoliation on park streams were dramatic increases in the concentration and export of N and base cations in streamwater. The elevated concentrations of NO_3^- in SHEN streams following defoliation did not appear to contribute to baseflow acidification in White Oak Run. This was due to a concurrent increase in concentrations of base cations in streamwater (Webb et al. 1995). Both NO_3^- and base cation concentrations increased during high-runoff conditions, although the increase in base cations did not fully compensate for the episodic increase in NO_3^- . Episodic acidification following defoliation thus became more frequent and more extreme in terms of observed minimum ANC (Webb et al. 1995). Following defoliation, NO_3^- export increased to previously unobserved levels and remained high for over six years before returning to pre-defoliation levels. Eshleman et al. (2001) estimated that park-wide export of NO_3^- in 1992, the year of peak defoliation, increased 1700% from a pre-defoliation baseline of about 0.1 kg/ha/yr. The very low pre-defoliation levels of NO_3^- export in park streams were consistent with expectations for N-limited, regenerating forests (Aber et al. 1989, Stoddard 1994). Release of NO_3^- to surface waters following defoliation was likewise consistent with previous observations of increased N export due to forest disturbance (Likens et al. 1970, Swank 1988). Webb et al. (1994) compared pre- and post-defoliation streamwater chemistry for 23 VTSSS watersheds. Nitrate concentrations, measured quarterly, increased in most of the streams in response to defoliation, typically by 10 to 20 $\mu\text{eq/L}$ or more.

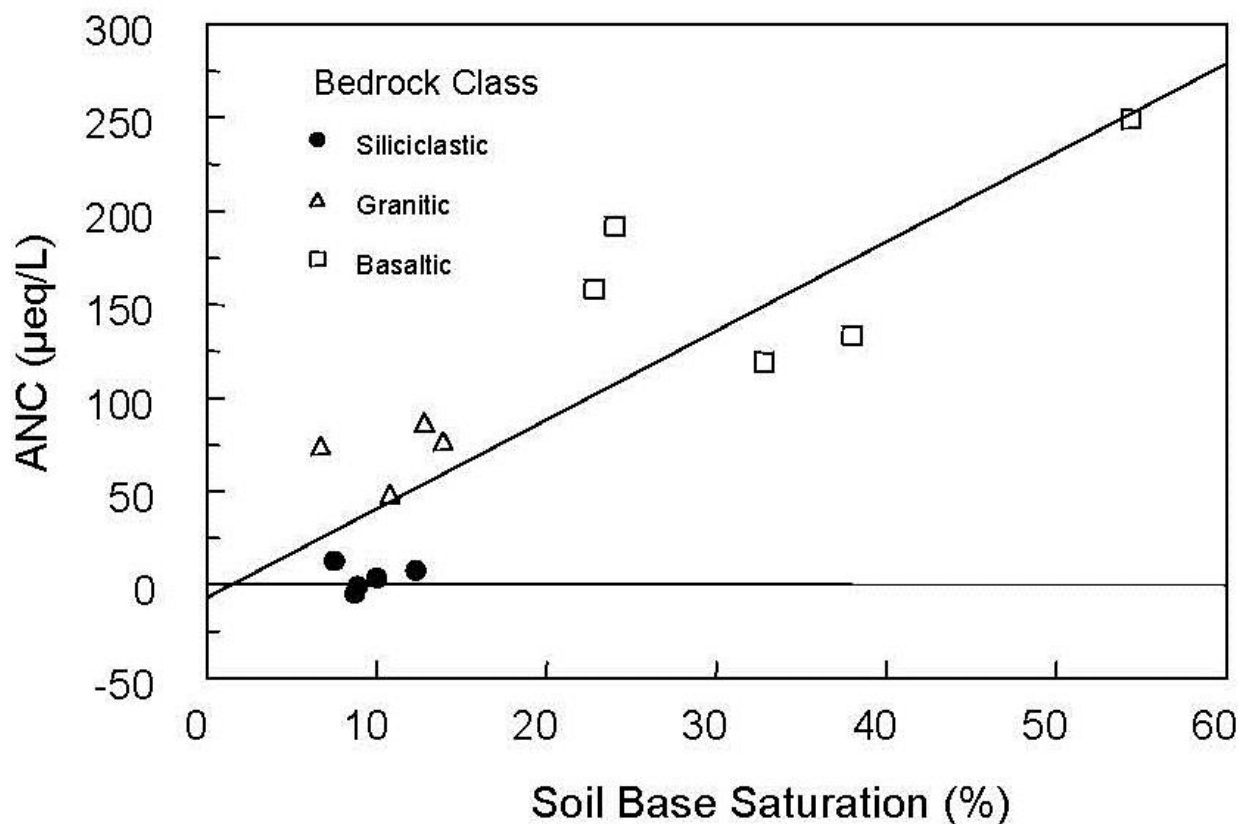


Figure 2. Median spring ANC of streams in SWAS watersheds during the period 1988 to 1999 versus median base saturation of watershed soils. Soils data were collected by the University of Virginia during the summer of 2000 (Welsch et al. 2001).

Jastram et al. (2013) synthesized data on surface water quality and aquatic biota in SHEN during the period 1979 to 2009. The effort focused on stream chemistry, benthic macroinvertebrates, and fish. Long-term trends in stream ANC suggested some improvements, but such increases in stream ANC were minimal for the most sensitive and impacted streams, which are located on siliciclastic bedrock. The watersheds having greater proportions of siliciclastic and granitic geology, with smaller size and higher minimum elevation, were generally experiencing continued degradation in stream acid-base chemistry. Trends in benthic macroinvertebrates generally suggested declines in stream condition over time. The streams on siliciclastic bedrock showed the lowest fish species richness and exhibited no evidence of recent recovery.

Eshleman et al. (1998) reported NO_3^- outputs from five small ($< 15 \text{ km}^2$) forested watersheds in Virginia (including within SHEN) and Maryland from 1988 to 1995. The study watersheds varied in geology, vegetation, and acid sensitivity, with baseflow ANC typically ranging from 0 to 10 $\mu\text{eq/L}$ in Paine Run to 150 to 350 $\mu\text{eq/L}$ in Piney River. Oak species (*Quercus* spp.), which are a preferred food source of gypsy moth larvae, occupied about 60% to 100% of the study watersheds. Nitrate concentrations increased in at least three of the watersheds in association with intense defoliation

during the late 1980s to early 1990s, to peak annual average NO_3^- concentrations in stream water of about 30 to 55 $\mu\text{eq/L}$. Most of the increased NO_3^- leaching occurred during storm flow conditions.

The increased streamwater NO_3^- concentration was probably derived largely from the N content of the foliage that had been consumed by the gypsy moth larvae and converted to feces on the forest floor (Webb 2004). Sulfate concentrations and ANC also decreased in streamwater. Although the mechanism for decreased SO_4^{2-} was not totally clear, Webb et al. (1994) hypothesized that increased nitrification in response to the increased soil N pool may have caused soil acidification, which would be expected to have increased soil S adsorption (cf., Johnson and Cole 1980). Decreased S deposition during the comparison period may also have contributed to the SO_4^{2-} response.

The full effect of the gypsy moth on aquatic resources in SHEN is not well understood. One consequence may be a reduction in the supply of available soil base cations and associated effects on streamwater ANC. Repeated periods of defoliation would probably increase the effect of episodic acidification on sensitive aquatic fauna and may determine the conditions under which some species are lost. Ultimately such effects may depend upon both the severity of future gypsy moth or other insect outbreaks and possibly on the amount of atmospheric N deposition. Gypsy moth populations typically display a pattern of periodic outbreaks and collapse (Campbell 1981). It remains to be seen what the long-term response will be (Sullivan et al. 2003).

Research at SHEN has also contributed significantly to the development of predictive models of watershed response to future conditions. The *Model of Acidification of Groundwater in Catchments* (MAGIC; 1985a, Cosby et al. 1985b, 1985c) of watershed response was initially developed largely using data collected within SHEN. MAGIC was the principal model used by NAPAP to estimate future damage to lakes and streams in the eastern United States (NAPAP 1991, Thornton et al. 1990) and is the most widely used dynamic acid-base chemistry model in the United States and Europe (Sullivan 2000).

The U.S. EPA's NSS statistical frame (Kaufmann et al. 1991) was used to estimate the number and percentage of stream reaches in the SAMI region that were modeled by MAGIC to change their chemistry in response to various emissions control strategies under consideration by SAMI (Sullivan et al. 2002, Sullivan et al. 2004). Simulations were based on assumed constant future atmospheric deposition at 1995 levels and on three regional strategies of emissions controls provided by SAMI, based on the Urban to Regional Multiscale One-Atmosphere model (Odman et al. 2002). There was a small decline in the estimated length of projected acidic (ANC # 0) streams by 2040 from the least to the most restrictive emissions control strategy, but there was little difference in projected stream length in the other ANC classes as a consequence of adopting one or another emissions control strategy. However, projections of continued future acidification were substantially larger under a scenario in which S and N deposition were held constant into the future at the relatively high 1995 levels. Similarly, Turner et al. (1992) reported MAGIC model simulation results that suggested substantial acidification ($\sim 20 \mu\text{eq/L}$) of aquatic systems would occur in the southeastern United States if deposition remained constant at 1985 levels.

The SAMI emissions control strategies used in the modeling of Sullivan et al. (2002, 2004) represented air regulatory requirements being implemented at the time of SAMI's formation, expected reductions under recent federal regulatory actions, and additional emissions controls applied to all emissions sectors in the eight SAMI states. The spatial variability of these emissions controls resulted in varying estimated future changes in S and N deposition at different locations within the SAMI region. The SAMI strategies were designated A2, B1, and B3. The A2 strategy was the reference strategy that represented SAMI's best estimates for air emission controls under regulations for which implementation strategies were relatively certain at the time of the study (about the year 2000). Emissions reductions under the A2 strategy included acid rain controls under Title IV of the 1990 Amendments to the CAA, the 1-hour O₃ standard, NO_x reductions required under EPA's call for revised State Implementation Plans (SIPs), and several highway vehicle and fuel reductions. The A2 strategy was applied for all eastern states and focused on the utility and highway vehicle sectors. The B1 and B3 strategies assumed progressively larger emissions reductions, targeted only to the eight SAMI states but covering all emissions sectors.

Streams exhibited a broad range of response to the cumulative S deposition loadings received to date and the large simulated decreases in S deposition in the future under the assumed emissions control strategies. Some streams showed modeled stream water SO₄²⁻ concentrations increasing in the future, even as S deposition was reduced by more than two-thirds. These were mostly sites that had relatively low SO₄²⁻ concentrations in 1995 ($\leq$ about 50 $\mu\text{eq/L}$) because of S adsorption on soils. They generally showed simulated future acidification, which was most pronounced for the A2 strategy. Other streams were simulated to show relatively large decreases in future stream water SO₄²⁻ concentrations and concurrent increases in ANC in response to the strategies, with progressively larger changes from the A2 to the B3 strategy. These tended to be streams that had relatively high concentrations of SO₄²⁻ ($>$ 50 $\mu\text{eq/L}$) in 1995, suggesting that they were closer to steady-state with respect to S inputs and outputs. Some streams were projected to exhibit future decreases in both SO₄²⁻ and NO₃⁻ concentrations but nevertheless to continue to acidify. This response was attributed by Sullivan et al. (2004) to large simulated decreases in base cation concentrations at these sites due to soil base cation depletion.

Most simulated changes in stream water ANC from 1995 to 2040 were rather modest, given the very large estimates of decreased S deposition in the simulations. Few modeled streams showed projected change in ANC of more than about 20 $\mu\text{eq/L}$. Some of the largest changes were simulated for some of the streams that were most acidic in 1995. For such streams, however, even relatively large increases in ANC would still result in negative ANC stream water, and therefore little biological benefit would be expected from the simulated improvement in chemistry. The model results suggested, however, that benefits would continue to accrue well beyond 2040 for all strategies, even if deposition was held constant at 2040 levels into the future.

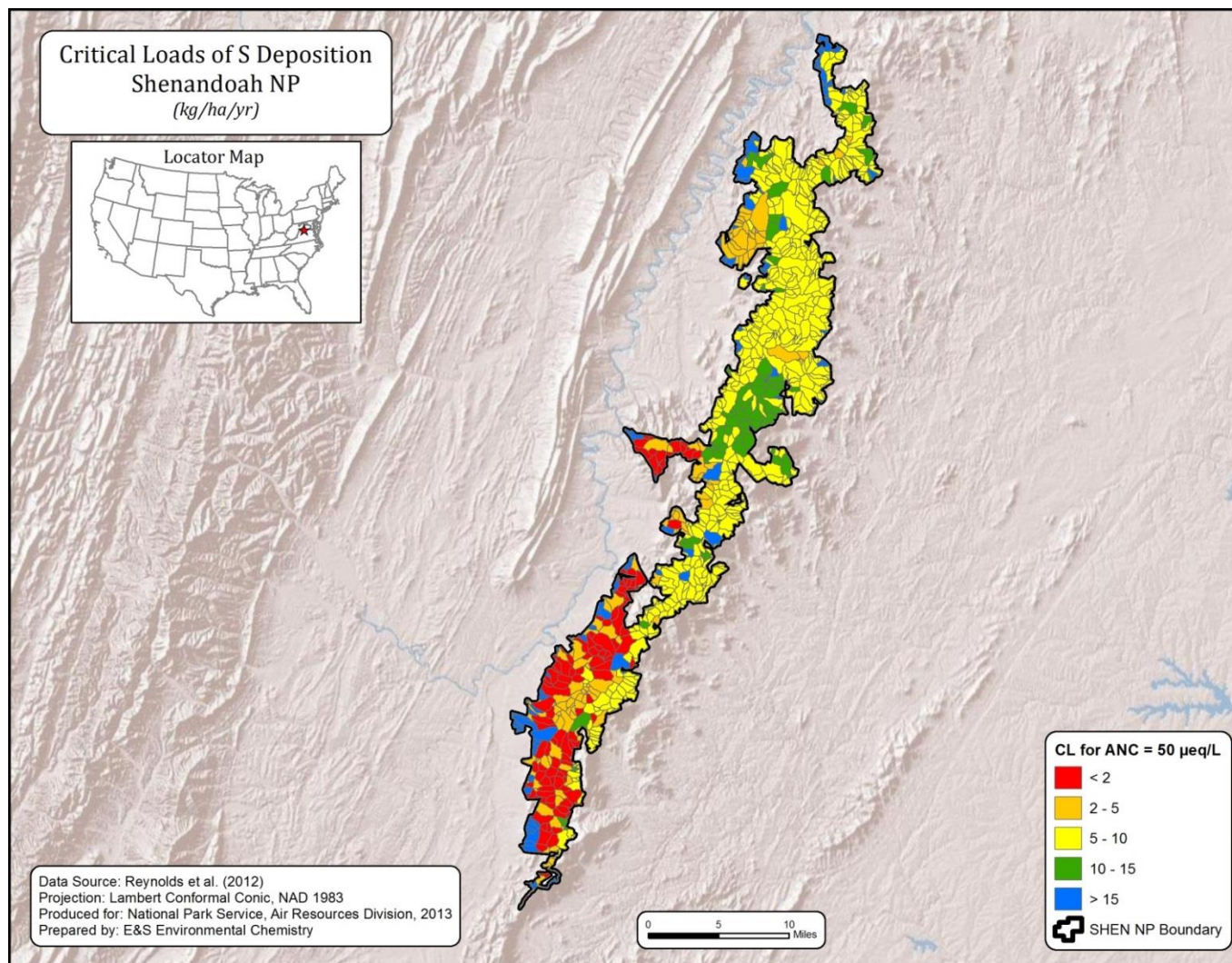
Measured stream chemistry in SHEN also shows relatively minor recovery in response to reductions in S emissions and deposition, in agreement with the SAMI simulation results. Sulfur deposition declined by about 40% between 1985 and 2000 in western Virginia, yet the acid-base chemistry of 65 monitoring stream sites showed no significant regional trends in stream ANC. For the subset of 14

monitoring sites in SHEN, Webb et al. (2004) found median decreases in stream SO_4^{2-} concentration and ANC of -0.229 and -0.168 $\mu\text{eq/L/yr}$, respectively. These recovery trends were very small relative to regional deposition reductions, estimates of historical acidification, and concurrent recovery at acid-sensitive surface water sites in the northeastern United States (Webb et al. 2004).

The steady-state CL for protecting streamwater ANC to a level of 50 $\mu\text{eq/L}$ in SHEN was modeled by Reynolds et al. (2012) and McDonnell et al. (2014) in the Ecosystem Management Decision Support (EMDS) study. Calculations were based on the Steady State Water Chemistry (SSWC) model, with the weathering parameter extrapolated from MAGIC model calibrations to the full study area. Results are given in Map 9 and Table 4. Model-predicted CL to protect and restore the ANC of streams in SHEN to 50 $\mu\text{eq/L}$ varied from largely in the range of ≤ 5 kg S/ha/yr in the southwestern portion of SHEN to the range of 5-10 kg S/ha/yr in the northern sections of the park. The median CL in SHEN was 7 kg S/ha/yr. Much of the central portion of the park was estimated to have CL less than 5 kg S/ha/yr and some areas were estimated to have S CL below 2 kg S/ha/yr, which is likely near the background preindustrial level of atmospheric S input to this park. This result suggests that Ca and other soil base cations may have become sufficiently depleted in portions of SHEN and surrounding areas that stream ANC will not increase to the target level of 50 $\mu\text{eq/L}$, even if S deposition is decreased to near-background levels. The CL values calculated by McDonnell et al. (2014) were uniformly high for streams in BOWA.

Temporal Variability in Water Chemistry

Acidic deposition can contribute to both chronic (long-term) and episodic (short-term) decline in streamwater ANC. Decreases in ANC and pH with increases in flow are nearly ubiquitous in drainage waters throughout the United States (Wigington et al. 1990). Chemical changes during episodes are controlled in part by acidic deposition and in part by natural processes, including dilution of base cation concentrations, nitrification, and flushing of organic acids from terrestrial to aquatic systems. Episodic acidification pulses may last for hours to weeks, and sometimes result in depletion of ANC in acid-sensitive streams and lakes to negative values and concomitant increases in inorganic aluminum (Al_i) in solution to toxic levels.



Map 9. Steady-state critical load of atmospheric S deposition for maintaining streamwater ANC at or above 50 µeq/L in SHEN. Estimates were generated within the Ecosystems Management Decision Support modeling effort of Reynolds et al. (2012) and McDonnell et al. (2014).

Table 4. Distribution of steady-state critical loads of sulfur (in kg/ha/yr) to protect stream ANC = 50 µeq/L for parks modeled in the EMDS project within the MIDN (McDonnell et al. 2014).

Park Name ¹	Park Code	# of CLs ²	Minimum	25th Percentile	Median	25th Percentile	Maximum
Booker T. Washington	BOWA	4	High	High	High	High	High
<i>Shenandoah</i>	SHEN	1072	0	4	7	9	High

¹ Park names are printed in bold italic for parks larger than 100 mi²

² Number of small watersheds (generally approximately 1 km²), for which CL were calculated by Reynolds et al.(2012), that are wholly or partly within the park

0 signifies that the target ANC cannot be attained, even if S deposition is reduced to zero

"High" signifies that the CL is significantly higher than ambient deposition

CLs of S in units of kg/ha/yr can be converted to meq/m²/yr by multiplying by 6.25

The degree to which acidic deposition results in chronic loss of ANC in streams within SHEN depends mainly upon two watershed processes associated with acid-base status: 1) acid anion retention in watershed soils; and 2) base-cation release from watershed soils and rocks (Church et al. 1992, Elwood et al. 1991). The degree to which acidic deposition results in episodic loss of ANC in surface water depends largely upon the hydrologic flow paths associated with high-runoff conditions (Turner et al. 1990, Wigington et al. 1990). These pathways largely determine the extent of acid neutralization provided by the soils and bedrock in that watershed. High-elevation watersheds with steep topography, extensive areas of exposed bedrock, deep snowpack accumulation, and shallow, base-poor soils tend to be most sensitive to episodic acidification. Such watershed features are common within SHEN and elsewhere in the MIDN. Episodic acidification in the MIDN is often the limiting condition for aquatic organisms in streams that can be suitable for aquatic life under baseflow conditions (cf., Wigington et al. 1993).

During high flows associated with snowmelt or rainfall events, flow-routing favors water flowpaths through upper horizons. During such events, drainage water chemistry typically reflects the lower pH, higher organic content, and lower ANC of these upper soil horizons (Sullivan 2000). Subsurface contact contributes to increased surface water ANC (Turner et al. 1990). As such, storm flow and snowmelt are often drivers of episodes of surface water acidity due to an increase in the proportion of flow derived from water that has moved laterally through the surface soil without infiltration to deeper soil horizons (Wigington et al. 1990).

Episodes are generally accompanied by changes in at least two or more of the following chemical parameters: ANC, pH, base cations, SO₄²⁻, NO₃⁻, Al_n⁺, organic acid anions, and DOC (Sullivan 2000). Episodic processes are mostly natural. Nevertheless, SO₄²⁻ and NO₃⁻ attributable to atmospheric deposition can play important roles in the episodic acidification of some surface waters in SHEN: by supplying N which can produce pulses of NO₃⁻ during high flow periods, contributing

hydrologically mobile SO_4^{2-} , and by lowering baseline pH and ANC, so that episodes are sufficient to produce biologically harmful conditions (Stoddard et al. 2003). The documented importance of NO_3^- to episodic acidification in SHEN streams was attributed to the effects of gypsy moth infestation in many watersheds within SHEN (Eshleman et al. 1999, Webb et al. 1995). Eshleman et al. (1999) hypothesized that the results of N effects studies in the park could largely be explained by a biogeochemical response to forest disturbance by gypsy moth larvae, which temporarily overwhelmed the normal controls on N and base cation dynamics.

A number of studies of episodic acidification have been conducted in streams within SHEN. Miller-Marshall (1993) analyzed data from the SWAS for the period 1988-1991 for White Oak Run, North Fork Dry Run, Deep Run, and Madison Run, and also conducted a field experiment in 1992 at White Oak Run and North Fork Dry Run. Acid anion flushing was identified as the predominant acidification mechanism during hydrological episodes. Base cation dilution frequently also played a large role, depending on the underlying bedrock geology and baseflow ANC. The ratio of $\Delta\text{SBC}/\Delta\text{ANC}$ varied from 0.5 at Madison Run (median spring baseflow ANC = 63 $\mu\text{eq/L}$) to -1.4 at Deep Run (median spring baseflow ANC = 1 $\mu\text{eq/L}$). Ratios were intermediate (0.2 and 0.3, respectively) at North Fork Dry Run (median spring baseflow ANC = 40 $\mu\text{eq/L}$) and White Oak Run (median spring baseflow ANC = 16 $\mu\text{eq/L}$). At the site exhibiting the lowest baseflow ANC (Deep Run), base cations increased during episodes. At the other sites, base cation concentrations were diluted during episodes, with the greatest dilution occurring in the streams that were highest in baseflow ANC (Miller-Marshall 1993).

Data regarding episodic variability in streamwater ANC for six intensively studied sites within SHEN for the period 1993 to 1999 are presented in Figure 3. The minimum measured ANC each year at each site (which generally is recorded during a large rain or snowmelt episode) is plotted against the median spring ANC for that year at that site. Sites that exhibited median spring ANC below about 20 $\mu\text{eq/L}$ (Paine Run, White Oak Run, Deep Run) generally had minimum measured ANC about 10 $\mu\text{eq/L}$ lower than median spring ANC.

In contrast, at the high-ANC Piney River site (median spring ANC > 150 $\mu\text{eq/L}$), the minimum measured ANC was generally more than about 40 $\mu\text{eq/L}$ lower than the respective median spring ANC. At sites having intermediate ANC values, with median spring ANC in the range of about 30 to 90 $\mu\text{eq/L}$, the minimum ANC measured each year was generally about 20 to 30 $\mu\text{eq/L}$ lower than the respective median spring ANC. Thus, there is a rather clear pattern in SHEN of larger episodic ANC depressions in streams having higher median ANC and smaller episodic ANC depressions in streams having lower median ANC. The two sites that had median spring ANC between about 0 and 10 $\mu\text{eq/L}$ consistently showed minimum measured values below 0.

The minimum ANC values that occurred in response to high flow were related to baseflow ANC values. This result is consistent with observations of Eshleman (1988). Paine Run (siliciclastic bedrock) had a mean weekly ANC value of about 6 $\mu\text{eq/L}$ and often had high-flow ANC values that were less than 0 $\mu\text{eq/L}$. Staunton River (granitic bedrock) had a mean weekly ANC value of about 82 $\mu\text{eq/L}$ and had only a few high-flow ANC values less than 50 $\mu\text{eq/L}$. Piney River (basaltic bedrock) had a mean weekly ANC value of 217 $\mu\text{eq/L}$ and no values as low as 50 $\mu\text{eq/L}$.

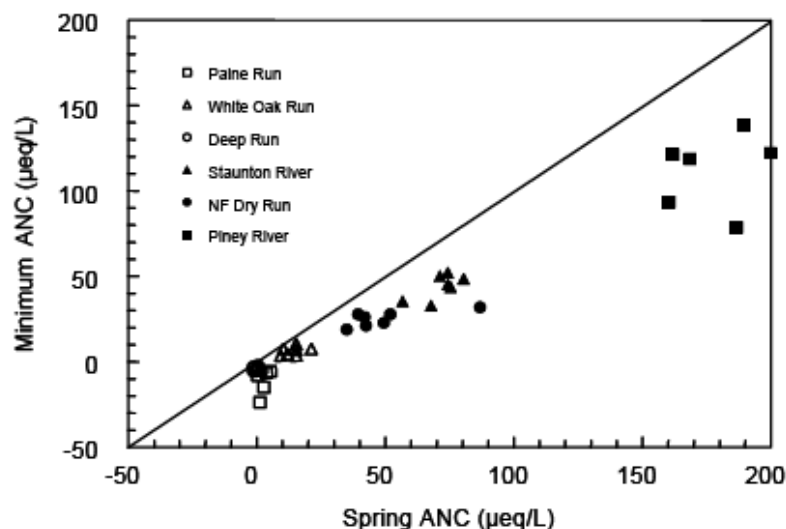


Figure 3. Minimum streamwater ANC sampled at each site during each year versus median spring ANC for all samples collected at that site during that spring season. Data are provided for all intensively-studied streams within SHEN during the period 1993-1999. A 1:1 line is provided for reference. The vertical distance from each sample point upwards to the 1:1 line indicates the ANC difference between the median spring value and the lowest sample value for each site and year. Source: Sullivan et al. (2003)

Eshleman and Hyer (2000) estimated the contribution of each major ion to observed episodic ANC depressions in Paine Run, Staunton River, and Piney River during a three-year period. During the study, 33 discrete storm events were sampled and water chemistry values were compared between antecedent baseflow and the point of minimum measured ANC (near peak discharge). The relative contribution of each ion to the ANC depressions was estimated using the method of Molot et al. (1989), which normalized the change in ion concentration by the overall change in ANC during the episode. At the low-ANC (~ 0 $\mu\text{eq/L}$) Paine Run site on siliciclastic bedrock, increases in NO_3^- and SO_4^{2-} , and to a lesser extent organic acid anions, were the primary causes of episodic acidification. Base cations tended to compensate for most of the increases in acid anion concentration. ANC declined by 3 to 21 $\mu\text{eq/L}$ (median 7 $\mu\text{eq/L}$) during the episodes studied.

At the intermediate-ANC (~ 60 to 120 $\mu\text{eq/L}$) Staunton River site on granitic bedrock, increases in SO_4^{2-} and organic acid anions, and to a lesser extent NO_3^- , were the primary causes of episodic acidification. Base cation increases compensated these changes to a large degree, and ANC declined by 2 to 68 $\mu\text{eq/L}$ during the episodes (median decrease in ANC was 21 $\mu\text{eq/L}$).

At the high-ANC (~ 150 to 200 $\mu\text{eq/L}$) Piney River site on basaltic (69%) and granitic (31%) bedrock, base cation concentrations declined during episodes (in contrast with the other two sites where base cation concentrations increased). Sulfate and NO_3^- usually increased. The change in ANC during the episodes studied ranged from 9 to 163 $\mu\text{eq/L}$ (median 57 $\mu\text{eq/L}$; Eshleman and Hyer

2000). Changes in base cation concentrations during episodes contributed to the ANC of Paine Run, had little effect in Staunton River, and consumed ANC in Piney River (Hyer 1997).

In general, pre-episode ANC is a good predictor of minimum episodic ANC and also a reasonable predictor of episodic change in ANC in SHEN streams. Higher values of pre-episode ANC contributed to larger changes in ANC values during episodes, but minimum ANC values of such streams were generally not especially low. Lowest minimum ANC values were reached in streams that had low pre-episode ANC, but the changes in ANC values for such streams were generally small.

A study by Deviney et al. (2006) used hourly ANC predictions over short time periods to compute recurrence intervals of annual water-year minimum ANC values for periods of 6, 24, 72, and 168 hours. They extrapolated the results to SHEN catchments using catchment geology and topography. Results suggested that many SHEN streams had 6- to 168-hour periods of low ANC values, which would stress resident fish populations (Deviney et al. 2006). On the basis of a 4-year recurrence interval, approximately 23% of the land area (44% of the catchments) would be expected to have conditions that are indeterminate (ANC 20 to 50 $\mu\text{eq/L}$), episodically acidic (ANC 0 to 20 $\mu\text{eq/L}$) or chronically acidic (ANC less than 0 $\mu\text{eq/L}$) for 72 continuous hours. Many catchments were predicted to have successive years of low-ANC values potentially sufficient to extirpate some species (Deviney et al. 2006). The authors of the study reported that smaller catchments were more vulnerable to episodic acidification than large catchments underlain by the same bedrock. Catchments with similar topography and size were estimated to be more vulnerable if underlain by less basaltic and carbonate bedrock.

Webb et al. (1994) developed an approach to calibration of an episodic acidification model for VTSSS long-term monitoring streams in western Virginia that was based on the regression method described by Eshleman (1988). Median spring quarter ANC concentrations in stream water for the period 1988 to 1993 were used to represent chronic ANC, from which episodic ANC was predicted. Regression results were very similar for the four lowest ANC watershed classes, and they were therefore combined to yield a single regression model to predict the minimum measured ANC from chronic ANC. Extreme ANC values were about 20% lower than chronic values, based on the regression equation:

$$\text{ANC}_{\min} = 0.79 \text{ANC}_{\text{chronic}} - 5.88 \text{ (} r^2=0.97; \text{ SE of slope}=0.02, \text{ p}=0.001 \text{)}$$

Because the model was based on estimation of the minimum ANC measured in the quarterly sampling program, it is likely that the true minimum ANC values were actually somewhat lower than 20% below the measured chronic ANC. Nevertheless, regression approaches for estimation of the minimum episodic ANC of surface waters, such as was employed by Webb et al. (1994) for western Virginia, provide a basis for predicting future episodic acidification. It must be recognized, however, that future episodic behavior might vary from current behavior if chronic conditions change dramatically.

Rice et al. (2005) developed transfer function time series models to predict hourly stream ANC from discharge for five watersheds in SHEN. Results were extrapolated to all watersheds in the park. Results suggested that about 14% of park watersheds have 72-hour periods of average ANC below 0 $\mu\text{eq/L}$ at least once every two years.

Thus, episodic acidification of streams in SHEN can be attributed to a number of causes, including dilution of base cations and flushing of NO_3^- , SO_4^{2-} and/or organic acids from forest soils to drainage water (Kahl et al. 1992, Lawrence 2002, Wigington 1999, Wigington et al. 1996). For streams having low pre-episodic ANC, episodic decreases in pH and ANC and increases in toxic Al concentrations can have adverse impacts on fish populations. Not all of the causes of episodic acidification are related to acidic deposition. Base-cation dilution and increase in organic acid anions during high-flow conditions are natural processes. The contribution of nitric acid, indicated by increased NO_3^- concentrations, has evidently been (at least for streams in the park) related to forest defoliation by the gypsy moth (Eshleman et al. 1998, Webb et al. 1995). However, significant contributions of sulfuric acid, indicated by increased SO_4^{2-} concentrations during episodes in some streams, is an effect of atmospheric deposition and the dynamics of S adsorption on soils (Eshleman and Hyer 2000).

Effects on Aquatic Biota

Aquatic biota in the MIDN have been affected by acidification at virtually all levels of the food web. Effects have been clearly documented for fish, aquatic insects, other invertebrates, and algae. Some species, and some life stages within species, are more sensitive than others. In some acidified waters, sensitive species have been eliminated and taxonomic richness has decreased. In some cases, all fish species have been eliminated from acidified waters.

Relatively little is known about sublethal changes in the condition of fish or other aquatic biota resulting from acidification in the MIDN. It is expected that sublethal effects will occur in acid-sensitive species well before the species is eliminated from a particular habitat. For that reason, loss of an acid-sensitive species is not necessarily an ideal indicator of acid stress. Clearly, stress begins to occur prior to species elimination. Sublethal effects are more difficult to quantify, but are nevertheless important.

Condition factor is one measure of sublethal effect that has been used to quantify impacts of acidification on fish. Condition factor is an index to describe the relationship between fish weight and length. Expressed as fish weight/length, multiplied by a scaling constant, this index reflects potential depletion of stored energy reserves (Dennis and Bulger 1995, Everhart and Youngs 1981, Goede and Barton 1990). Fish with higher condition factor are more robust than fish having lower condition factor.

Observed differences in condition factor may occur because maintenance of internal chemistry in the more acidic streams would require energy that otherwise would be available for growth and weight gain (Dennis and Bulger 1999, Webb 2003). The energy costs to fish for active iono-osmoregulation can be substantial (Bulger 1986, Farmer and Beamish 1969). Because of the steep gradient in sodium (Na^+) and chloride (Cl^-) concentrations between fish blood and freshwater, there is constant diffusional loss of these ions, which must be replaced by energy-requiring active transport. Low pH

increases the rate of passive loss of blood electrolytes (especially Na^+ and Cl^-), and dissolved Al elevates losses of Na^+ and Cl^- above the levels that occur due to acid stress alone (Wood 1989).

It is also possible that the loss of sensitive individuals or early life stages within species may reduce competition for food among the survivors, resulting in better growth rates, survival, or condition. Similarly, competitive release (increase in growth or abundance subsequent to removal of a competitor) may result from the loss of a sensitive species, with positive effects on the density, growth, or survival of competitor population(s) of other species (Baker et al. 1990b). However, in some cases where acidification continued, transient positive effects on size of surviving fish were shortly followed by extirpation (Bulger et al. 1993).

Field studies in the MIDN have shown lower condition factor in fish found in more acidic streams (Dennis and Bulger 1995, Webb 2003). Condition factor has been developed and applied mainly for blacknose dace (*Rhinichthys atratulus*). This species is widely distributed in Appalachian Mountain streams and is moderately tolerant of low pH and ANC, relative to other fish species in the region. Condition factor may be a useful metric for many species in aquatic ecosystems that are only marginally affected by acidification.

Bulger et al. (1999) observed a positive relationship between condition factor and pH in streams in SHEN (Figure 4). Dennis and Bulger (1995) found a reduction in the condition factor for blacknose dace in waters near pH 6.0. The four populations shown in Figure 4 with the lowest condition factor had mean stream pH values within or below the range of critical pH values at which Baker and Christensen (1991) estimated that negative population effects for blacknose dace are likely for the species. The mean length-adjusted condition factor of fish from the study stream with the lowest ANC was about 20% lower than that of the fish in best condition.

Acid stress is at least partly responsible for the low condition factor of many blacknose dace populations in SHEN, though reduced access to food or lower food quality (Baker et al. 1990b), either resulting from the nature of soft water streams or exacerbated by acidification, cannot be ruled out. Primary productivity is low in headwater streams and lower still in soft water headwaters, which are more likely to be acidified. Production of invertebrates is likely to be low in such streams as well (Wallace et al. 1992). Thus, lower food availability cannot be discounted as a potential contributor to lowered condition in blacknose dace populations in low-pH streams in SHEN.

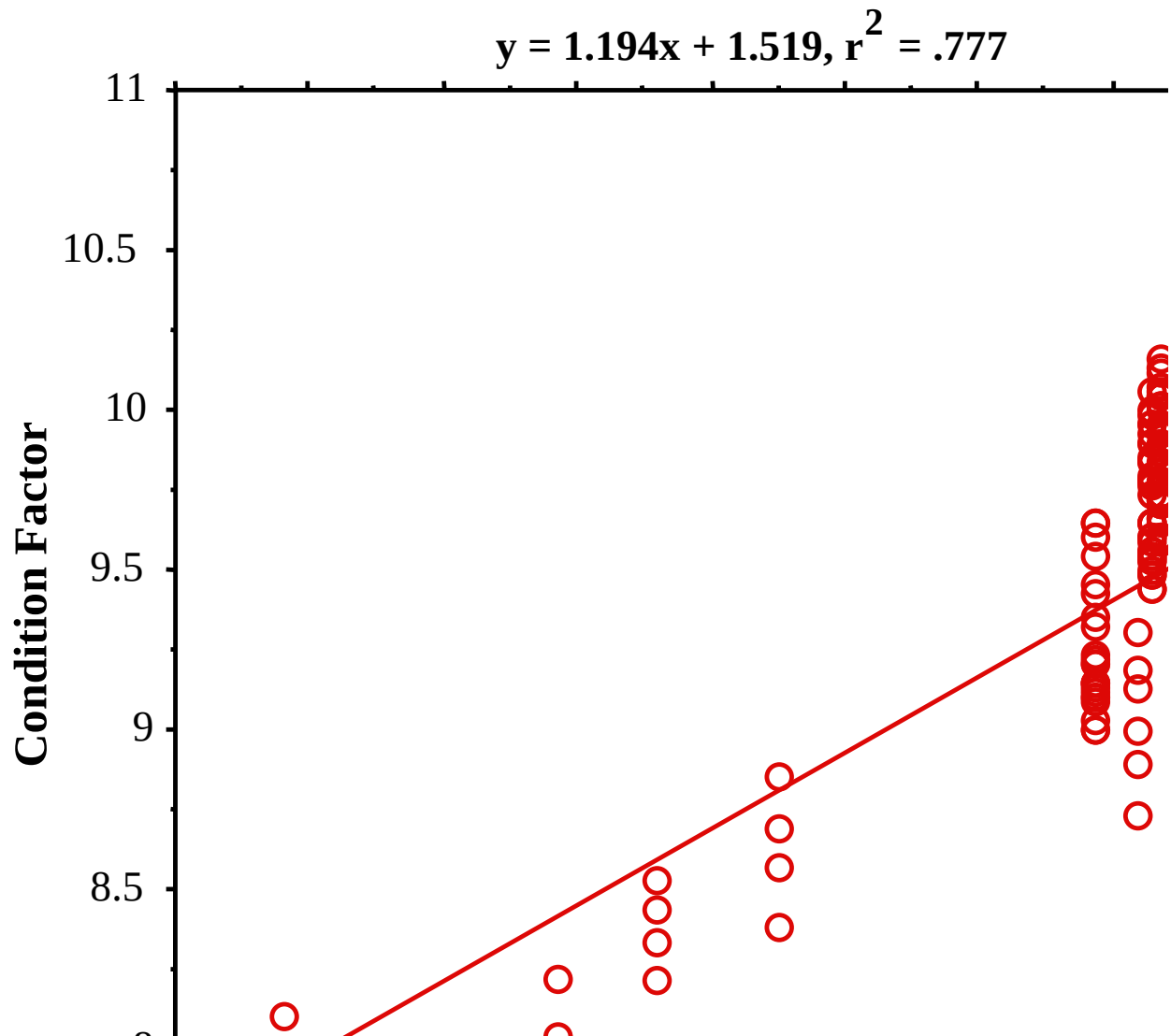


Figure 4. Length-adjusted condition factor (K), a measure of body size in blacknose dace compared with mean stream pH among 11 populations (n=442) in Shenandoah National Park. Values of pH are means based on quarterly measurements, 1991-94; K was measured in 1994. The regression analysis showed a highly significant relationship ($p < 0.0001$) between mean stream pH and body size, such that fish from acidified streams were less robust than fish from circumneutral streams. Source: (Bulger et al. 1999)

Taxonomic richness is a metric that is commonly used to quantify the effects of an environmental stress such as acidification. The richness metric can be applied at various taxonomic levels. For example, the number of fish species can be used as an index of acidification (cf., Bulger et al. 1999). Similarly, acidification effects on aquatic insects can be evaluated on the basis of the number of families or genera of mayflies (order Ephemeroptera; Sullivan et al. 2003).

Acidification results in the loss of acid-sensitive taxa, with more species lost in response to greater amounts of acidification in biota. A direct outcome of population loss caused by acidification is a decline in species richness (the total number of species in a stream). This is a highly predictable

outcome of regional acidification, although the pattern and rate of species loss varies from region to region.

Acidification is a conspicuous threat to three trout species in the MIDN region: brook trout, brown trout (*Salmo trutta*), and rainbow trout (*Oncorhynchus mykiss*). Although brown and rainbow trout are found within SHEN, brook trout predominate. Of the three, native brook trout is the most acid tolerant, brown trout introduced from Europe is intermediate in acid tolerance, and rainbow trout introduced from the western United States is most sensitive. The Southern Appalachian Man and the Biosphere (SAMAB 1996) survey concluded that trout populations are regarded by residents of the southern Appalachian Mountains region as among the region's most valuable aquatic natural resources, and trout populations and trout habitat are major concerns to the public in the southern Appalachians. Sources of concern generally fall into three categories: 1) fisheries for native brook trout and introduced rainbow and brown trout; 2) "existence value" for brook trout, regarded as a beautiful and intrinsically valuable native species; and 3) the presence of trout as indicators of high water quality.

The VTSSS surveyed streamwater chemistry for 344 (~80%) of the native brook trout streams in western Virginia (Webb et al. 1994). About half of the streams included in the VTSSS had ANC < 50 $\mu\text{eq/L}$. In contrast, the NSS (Kaufmann et al. 1988) data for western Virginia suggested that only about 15% of the streams in the NSS target population had ANC < 50 $\mu\text{eq/L}$. Webb et al. (1994) interpreted these differences as a reflection of the smaller watershed size, more mountainous topography, and generally more inert bedrock of the VTSSS sample watersheds, as compared with the overall NSS stream population. An estimated 18% of potential brook trout streams in the mid-Appalachian Mountains are too acidic for brook trout survival (Herlihy et al. 1996).

In SHEN, a statistically robust relationship between acid-base status of streams and fish species richness was documented. The three-year Fish in Sensitive Habitats (FISH) study of stream acidification in SHEN demonstrated negative effects on fish from both chronic and episodic acidification (Bulger et al. 1999). Biological effects in low- versus high-ANC streams included changes in species richness, population density, condition factor, age, size, and field bioassay survival. As an element of the FISH project (Bulger et al. 1999), numbers of fish species were compared among 13 SHEN streams spanning a range of pH and ANC conditions. There was a highly significant ($p < 0.0001$) relationship between stream acid-base status (during the 7-year period of record) and fish species richness among the 13 streams. The streams with the lowest ANC hosted the fewest species (Figure 5). The best fit regression line suggested, on average, a loss of one species for every 21 $\mu\text{eq/L}$ decline in annual minimum recorded ANC value. Both episodic and chronic mortality occurred in young brook trout in a low-ANC stream, but not in a high-ANC stream (MacAvoy and Bulger 1995). Blacknose dace in low-ANC streams were in poor condition relative to those in higher-ANC streams (Dennis and Bulger 1995, Dennis et al. 1995).

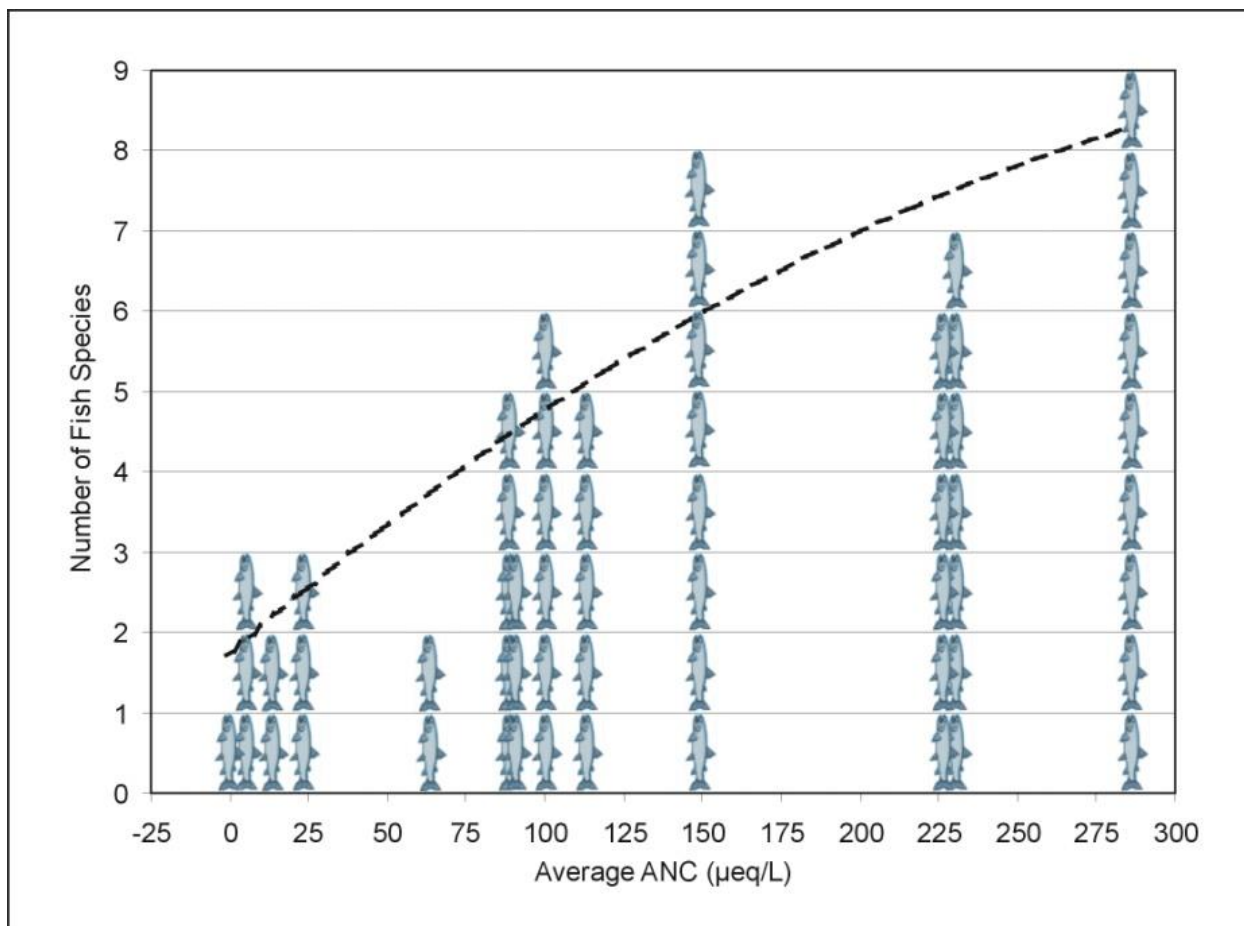


Figure 5. Number of fish species among 13 streams in SHEN. Values of ANC are means based on quarterly measurements, 1987-94. The regression analysis showed a highly significant relationship ($p < 0.0001$) between mean stream ANC and number of fish species. Streams having ANC consistently $< 75 \mu\text{eq/L}$ had three or fewer species. Source: Redrawn from Bulger et al. (1999)

Bulger et al. (2000) developed model-based projections using the MAGIC model to evaluate the potential effect of reductions in S deposition of 40% and 70% from 1991 levels using data from VTSSS and SWAS. Projections were based on four brook trout stream categories: Suitable, ANC $> 50 \mu\text{eq/L}$; Indeterminate, ANC 20 to $50 \mu\text{eq/L}$; Marginal, ANC 0 to $20 \mu\text{eq/L}$; and Unsuitable, ANC $< 0 \mu\text{eq/L}$. Three scenarios of future acidic deposition were modeled: constant deposition at 1991 levels, 40% reduction from 1991 deposition levels, and 70% reduction from 1991 deposition levels. Based on observed 1991 ANC values, approximately 30% of all trout streams in Virginia were marginal or unsuitable for brook trout because they were either episodically (24%) or chronically (6%) acidic. In addition, another 20% of the streams were classified as indeterminate, and brook trout in these streams may or may not have been affected. Based on the model simulations, 82% of these streams would not have been acidic prior to the onset of acidic deposition and would likely have been suitable for brook trout.

The model projections suggested that neither the 40% nor the 70% reductions in acidic deposition would be expected to increase the number of streams that were suitable for brook trout above the

ambient 50%. In fact, the results suggested that a 70% reduction in deposition would be needed in the long term just to maintain the number of streams that were considered suitable for brook trout. Because of the length of time required to restore buffering capacity in watershed soils, most of the marginal or unsuitable streams were expected to remain marginal or unsuitable for the foreseeable future.

Median stream ANC values and watershed areas are shown in Table 5 for the streams used by Bulger et al. (1999) to develop the relationship between ANC and fish species richness shown in Figure 5. Despite the overall similarities, these study streams vary in watershed area by a factor of 10, and this can affect the fish species richness. It appears that fish species richness is controlled by multiple factors, of which both acidification and watershed area can be important. Watershed area might be important in this context because smaller watersheds may contain smaller streams having less diversity of habitat, more pronounced effects on fish from high-flow conditions, or lower food availability. The streams that have larger watershed area generally have more fish species than the streams having smaller watershed area. All of the "rivers" have watersheds larger than 10 km² and ANC higher than 75 µeq/L. In contrast, the majority (but not all) of the "runs" have watershed area smaller than 10 km² and ANC less than 20 µeq/L. All of the streams that have watershed areas smaller than 10 km² have three or fewer known species of fish present. All of the streams having larger watersheds (> 10 km²) have three or more known fish species; seven of nine have five or more species; and the average number of fish species is six. There is no clear distinction between river and run, but it is clear that as small streams in SHEN combine and flow into larger streams and eventually to rivers, two things happen: acid-sensitivity generally declines, and habitat generally becomes suitable for additional fish species (Sullivan et al. 2003).

Table 5. Median streamwater ANC and watershed area of streams in SHEN that have water chemistry and fish species richness data.

Site ID	Watershed Area (km ²)	Median ANC (µeq/L)	Number of Fish Species
Smaller Watersheds (< 10 km ²)			
North Fork Dry Run	2.3	48.7	2
Deep Run	3.6	0.3	N.D. ¹
White Oak Run	4.9	16.2	3
Two Mile Run	5.4	10.0	2
Meadow Run	8.8	-3.1	1
Larger Watersheds (> 10 km ²)			
Brokenback Run	10.1	74.4	3
Staunton River	10.6	76.8	5
Piney River	12.4	191.9	7
Paine Run	12.7	3.7	3
Hazel River	13.2	86.8	6
White Oak Canyon	14.0	119.3	7
N. Fork Thornton River	18.9	249.1	9
Jeremy's Run	22.0	158.5	6
Rose River	23.6	133.6	8

¹ No data were available regarding the number of fish species in Deep Run.

In order to develop projections of probable past and future responses of aquatic biota to changing S deposition in SHEN, the MAGIC model was coupled by Sullivan et al. (2003) with several empirical models which linked biological response to past and future model projections of water quality. Unlike MAGIC, which is a geochemical process-based model, the biological effects estimates were based on observed empirical relationships rooted in correlation and expressed as linear relationships. Correlation does not necessarily imply causality, but an observed pattern of co-variation between variables does provide a quantitative context for extrapolation. In this case, the projections did not require extrapolation beyond the observed ranges of observations, and therefore the projections were statistically robust. To the extent that the observed empirical relationships used in the coupled models do in fact reflect the effects of acid stress on aquatic biota, the projections were also biologically robust.

Dynamic water chemistry model projections were combined with biological dose-response relationships to estimate declines in fish species richness with acidification. A relationship derived from the data in Figure 5 was used by Sullivan et al. (2003) with stream ANC values predicted by the MAGIC model to provide estimates of the expected number of fish species in each of the modeled streams for the past, present, and future chemical conditions simulated for each stream. The coupled geochemical and biological model predictions were evaluated by comparing the predicted species richness in each of the 13 streams with the observed number of species that occurred in each stream.

The agreement between predicted and observed species numbers was good, with a root mean squared error (RMSE) of 1.2 species across the 13 streams. The average error was 0.3 species, indicating that the coupled models were unbiased in their predictions. Model reconstructions of past species richness in the streams suggested that historical loss of species had been greatest in the streams located on the most sensitive geological class (siliciclastic). The average number of species lost from streams on the three bedrock types examined were estimated as: 1.6 species on siliciclastic bedrock; 0.4 species on granitic bedrock; and 0.4 species on basaltic bedrock (Sullivan et al. 2003). In the case of the siliciclastic streams, the projected past changes were much larger than the average error and RMSE of the coupled models.

For SHEN, Bulger et al. (1999) concluded that the most important cause of the observed decline in fish species richness with decreasing ANC was acid stress associated with acidification. However, an additional causal factor may have been the decrease in the number of available aquatic niches when moving from downstream locations (which are seldom low in pH and ANC) to upstream locations (which are often low in pH and ANC in this region; Sullivan et al. 2003). The relative importance of this latter factor, compared with the importance of acid stress, in determining this relationship is not known.

South of SHEN the effects of surface water acidification on fish species richness have been studied in some detail in the St. Mary's River, which is also in Virginia. Fish species richness was closely associated with surface water acid-base chemistry. Bugas et al. (1999) conducted electrofishing in the St. Mary's River in 1976, and every 2 years from 1986 through 1998. Systemic stream acidification occurred during the study period. Sampling occurred at six sites between the downstream end of the St. Marys Wilderness and the headwaters over a distance of about 8 km. The number of fish species in the St. Marys River within the wilderness declined from 12 in 1976 to 4 in 1998. Three of the four species present in 1998 (brook trout, blacknose dace, fantail darter [*Etheostoma flabellare*]) are relatively tolerant of low pH and are typically the only fish species present in streams having similar levels of acidity in nearby SHEN (Bulger et al. 1999, Webb 2003). Bugas et al. (1999) reported that successful brook trout reproduction in the St. Marys River occurred only 1 year out of 4 during the period 1995 through 1998. Eight of the fish species recorded in one or more early years were not observed in more recent years. Several, including blacknose dace, rainbow trout, and torrent sucker (*Thoburnia rhotoca*), showed a pattern of being progressively restricted over time to lower river reaches, which generally had higher ANC.

MacAvoy and Bulger (1995) used multiple bioassays over 3 years in one of the low-ANC streams in SHEN as part of the FISH project to determine the effect of stream baseflow and episodic stream chemistry on the survival of brook trout eggs and fry. Simultaneous bioassays took place in mid- and higher-ANC reference streams. Acid episodes (with associated low pH and elevated Al_i concentrations, and high streamwater discharge) induced rapid mortality in the low-ANC stream, while the test fish in the higher-ANC stream survived (Bulger et al. 1999).

The southern Appalachian area is widely regarded as one of the most diverse landscapes in the Temperate Zone (SAMAB 1996). Fish diversity is quite high. There are about 950 freshwater fish species in North America (Jenkins and Burkhead 1993), of which about 485 species can be found in

the Southeast, about 210 species in Virginia (Jenkins and Burkhead 1993), and more than 30 species in SHEN. Regional habitat diversity and intraspecific genetic diversity are also regarded as high. Thus, the Southeast is a unique national biodiversity resource for fish. Unfortunately, the Southern Appalachian Assessment concluded that 70% of sampled stream locations showed moderate to severe fish community degradation, and that about 50% of the stream length in West Virginia and Virginia showed habitat impairment (SAMAB 1996).

Fish communities of high-gradient central and southern Appalachian streams may contain a variety of species, but are often dominated by trout, especially brook trout. There are clear patterns in species distribution from headwaters to rivers, which can also be seen in community comparisons among reaches at different elevations; the clearest pattern is that species richness increases in a downstream direction. This is thought to result from the rather small number of upstream species, which must tolerate simultaneously highest current velocities and lowest pH values. Fish are absent from the highest headwaters, where they are replaced by salamanders. The highest-elevation fish species is usually brook trout, typically joined downstream by dace (e.g., blacknose dace), a sculpin (e.g. mottled sculpin, *Cottus bairdi*) and a darter (e.g. fantail darter), and perhaps by introduced brown or rainbow trout (Wallace et al. 1992). In the context of acidification, the introduced trout are both more acid-sensitive than brook trout, and will not be present in acidified waters. Proceeding downstream, other dace, darters, chubs, shiners, suckers and others are often present (Wallace et al. 1992).

Results from the U.S. EPA's Episodic Response Project demonstrated that episodic acidification can have long-term adverse effects on fish populations. Streams with suitable chemistry during low-flow, but low pH and high Al levels during high flow, had substantially lower numbers and biomass of brook trout than were found in non-acidic streams (Wigington et al. 1996). Streams having acidic episodes showed significant mortality of fish. Some brook trout avoided exposure to stressful chemical conditions during episodes by moving downstream or into areas with higher pH and lower Al concentration. This movement of brook trout only partially mitigated the adverse effects of episodic acidification, however, and was not sufficient to sustain fish biomass or species composition at levels that would be expected in the absence of acidic episodes. These findings suggested that stream assessments based solely on chemical measurements during low-flow conditions will not accurately predict the status of fish populations and communities in small mountain streams unless some adjustment is made for episodic processes (Baker et al. 1990a, Baker et al. 1996, Wigington et al. 1996).

Effects on biota can be assessed as effects on a particular sensitive species or species perceived to be important, or as effects on the richness or diversity of fish or other potentially sensitive life form.

Table 6. Brook trout acidification response categories developed by Bulger et al. (2000) for streams in Virginia

Response Category	Chronic ANC Range (µeq/L)	Expected Response
Suitable	> 50	Reproducing brook trout expected if other habitat features are also suitable
Indeterminate	20 to 50	Brook trout response expected to be variable
Episodically acidic	0 to 20	Sub-lethal and/or lethal effects on brook trout are possible
Chronically acidic	< 0	Lethal effects on brook trout probable

ANC criteria have been used for evaluation of potential acidification effects on fish communities. The utility of these criteria lies in the association between ANC and the surface water constituents that directly contribute to or ameliorate acidity-related stress, in particular pH, Ca^{2+} , and Al. Bulger et al. (2000) developed ANC thresholds for brook trout response to acidification in forested headwater catchments in western Virginia (Table 6). Note that because brook trout are comparatively acid tolerant, adverse effects on many other fish species should be expected at relatively higher ANC values. These values were based on annual average stream water chemistry, and therefore represent chronic exposure conditions. The likelihood of additional episodic stress is incorporated into the response categories in the manner in which they are interpreted. For example, the episodically acidic response category, which has chronic ANC in the range of 0 to 20 µeq/L, represents streams which are expected to acidify to ANC near or below 0 during rainfall or snowmelt episodes. In such streams, sublethal and/or lethal effects on brook trout are possible (Bulger et al. 2000, Sullivan et al. 2003).

Fish species richness, population density, condition factor, age distribution, size, and bioassay survival have all been shown to be reduced in low-ANC streams as compared to intermediate-ANC and high-ANC streams (Bulger et al. 1995, Dennis and Bulger 1995, Dennis et al. 1995, MacAvoy and Bulger 1995). Fish species richness is a good indicator of acidification response. Lakes or streams having pH below about 5.0 or ANC below about 0 generally do not support fish. Depending on the region, waters having pH above about 6.5 and ANC above about 50 µeq/L support large, but variable, numbers of species. There is often a positive relationship between pH and number of fish species, at least for pH values between about 5.0 and 6.5, or ANC values between about 0 and 50 to 100 µeq/L (Bulger et al. 1999, Sullivan et al. 2006). Such observed relationships are complicated, however, by the tendency for smaller lakes and streams, having smaller watersheds, to also support fewer fish species, irrespective of acid-base chemistry. This pattern may be due to a decrease in the number of available niches as stream or lake size decreases. Nevertheless, fish species richness is one of the most useful indicators of biological effects of surface water acidification.

Streams with chronic ANC greater than about 50 µeq/L are generally considered suitable for brook trout in the southeastern United States because they have a large enough buffering capacity that persistent acidification poses no threat to this species, and there is little likelihood of storm-induced

acidic episodes lethal to brook trout. In such streams, reproducing brook trout populations are expected if the habitat is otherwise suitable (Bulger et al. 2000), although some streams may periodically experience episodic chemistry that affects species more sensitive than brook trout. Streams having annual average ANC from 20 to 50 $\mu\text{eq/L}$ may or may not experience episodic acidification during storms that can be lethal to juvenile brook trout, as well as other fish. Streams that are designated as episodically acidic (chronic ANC from 0 to 20 $\mu\text{eq/L}$) are considered marginal for brook trout because acidic episodes are likely (Hyer et al. 1995), although the frequency and magnitude of episodes vary. Streams that are chronically acidic (chronic ANC less than 0 $\mu\text{eq/L}$) are not expected to support healthy brook trout populations (Bulger et al. 2000).

Acidification also affects aquatic life forms other than fish. Within stream systems, macroinvertebrate communities are among the most sensitive life forms to disturbances, including those associated with atmospheric deposition (Cairns and Pratt 1993). In addition, they are relatively easy to sample in the field (Karr and Chu 1999, Plafkin et al. 1989, Potyondy et al. 2006, Resh et al. 1995). Considerable data are available for aquatic insects in SHEN and elsewhere in the central and southern Appalachian Mountains.

It has been well documented that low streamwater pH can be associated with reductions in invertebrate species richness or diversity (Burton et al. 1985, Hall and Ide 1987, Kimmel et al. 1985, Peterson and Van Eechhaute 1992, Raddum and Fjellheim 1984, Rosemond et al. 1992, Sullivan et al. 2003, Townsend et al. 1983), and sometimes density (Aston et al. 1985, Burton et al. 1985, Hall et al. 1980, Kimmel et al. 1985, Townsend et al. 1983). Effects on invertebrate density are not universal; a number of studies have found no density effects (Harriman and Morrison 1982, Ormerod and Tyler 1987, Simpson et al. 1985, Winterbourn and Collier 1987). However, a decrease in species richness with decreasing pH has been found in almost all such studies (Rosemond et al. 1992); decreases in pH of one unit or more typically result in species loss. Invertebrate taxa that are most sensitive to acidification are mayflies, amphipods, snails, and clams. For example, Porak (1981) found that all species of mayfly were intolerant of the acid condition in the streams containing acidic Anakeesta leachates. Caddisflies are also highly sensitive. At low levels of acidification (pH 5.5 to 6.0), acid-sensitive species are replaced by more acid-tolerant species, yielding little or no change in total community species richness, diversity, density or biomass. If pH decreases are larger, more species will be lost without replacement, resulting in decreased richness and diversity.

Possible mechanisms for acidification effects on invertebrates include direct toxicity of H^+ and Al , disruption of ion regulation, and reproductive failure. Indirect effects due to acidification-induced changes to invertebrate predator populations are also possible (Baker et al. 1990c). Acidic episodes in streams have been shown to cause increased downstream drift of acid-sensitive species, particularly *Baetis* spp. (Kratz et al. 1994, Smock and Gazzera 1996).

The Ephemeroptera-Plecoptera-Tricoptera (EPT) Index is a common measure of stream macroinvertebrate community integrity. The EPT metric is the total number of families present in those three insect orders (mayflies, stoneflies, and caddisflies, respectively). The total number of families is generally lower at acidified sites because species within those families tend to exhibit

varying acid sensitivity (cf., SAMAB, 1996). Mayflies tend to be most sensitive of the three, and stoneflies tend to be least sensitive (Peterson and Van Eechhaute 1992).

Benthic macroinvertebrates have been monitored in SHEN streams since 1986 and in the other MIDN parks since 2009 as part of the Long-Term Ecological Monitoring System (LTEMs). They have several characteristics that make them particularly useful for biomonitoring (Moeykens and Voshell 2002):

- Benthic macroinvertebrates occur in almost all types of freshwater habitats.
- There are many different taxa which include a wide range of sensitivity to environmental stress.
- They have mostly sedentary habits and are therefore likely to be exposed to ambient pollution or environmental stress.
- The duration of their life histories are sufficiently long such that they will likely be exposed to the environmental stress that is present, and the community will not recover so quickly that the impact will go undetected.
- Sampling the benthic macroinvertebrate assemblage is relatively simple and does not require complicated equipment or great effort.
- Taxonomic identification is almost always easy to the family level and usually easy to the genus level.

Since 1986, the benthic macroinvertebrate community at 17 core LTEMs sites in SHEN has been sampled at least once per year, and in 1995 SHEN personnel began to sample other sites with the goal of eventually sampling every permanent stream within park boundaries (Moeykens and Voshell 2002). The sampling techniques and LTEMs protocols were described by Voshell and Hiner (1990).

Nutrient Nitrogen Enrichment

The vegetation types thought to be most responsive to nutrient N enrichment effects (arctic, alpine, grassland and meadow, wetland, and arid and semi-arid) are generally absent from SHEN. There are some areas of meadow and wetland in SHEN, including Big Meadows, but they constitute a small percentage of the park resources. Meadows and wetlands are somewhat more common in the other MIDN parks.

The network rankings developed by Sullivan et al. (2011a) for a coarse screening assessment of nutrient N Pollutant Exposure, Ecosystem Sensitivity to nutrient N enrichment, and Park Protection yielded an overall network nutrient N enrichment Summary Risk ranking for the MIDN that was near the top of the third quintile among all networks. The overall level of concern for nutrient N enrichment effects on I&M parks within the MIDN was judged by Sullivan et al. (2011a) to be Moderate.

SHEN was ranked by Sullivan et al. (2011a) near the top among parks in nutrient N Pollutant Exposure, but in the lowest quintile (Very Low) in Ecosystem Sensitivity to nutrient N enrichment (Table 7), being largely forested. There are also no high-elevation lakes in SHEN that might be particularly sensitive to N-based eutrophication.

Most of the smaller historical parks in the MIDN were ranked Very High in nutrient N Pollutant Exposure by Sullivan et al. (2011a); the exceptions were APCO, which was ranked High and BOWA, which was ranked Moderate (Table 7). The smaller parks were variable in Ecosystem Sensitivity to nutrient N enrichment, from Very Low in BOWA and PETE to High in VAFO (Sullivan et al. 2011a). Although rankings provide an indication of risk, park-specific data, particularly regarding nutrient-enrichment sensitivity, are needed to fully evaluate risk from nutrient N addition.

Although grassland and wetland plant community types are thought to be more sensitive to nutrient N enrichment than forested plant communities, N deposition can also affect nutrient dynamics in northern hardwood forests, which are common in SHEN. Hardwood forests found throughout the northeastern United States and south to Virginia appear to have experienced increased tree growth with increasing N deposition across a depositional gradient from about 3 to 11 kg N/ha/yr (Thomas et al. 2010). Observed tree growth responses were species-specific. Growth increases were most pronounced for red maple (*Acer rubrum*), sugar maple, white ash, yellow poplar (*Liriodendron* pine (*Pinus strobus*), quaking aspen (*Populus tremuloides*), northern red oak (*Quercus rubra*), and scarlet oak (*Q. coccinea*). Other tree species showed negative response to N addition. Growth decreased to a statistically significant level with increasing deposition for red pine (*Pinus resinosa*), red spruce, and northern white cedar (*Thuja occidentalis*). Mortality increased with increasing deposition for yellow birch (*Betula alleghaniensis*), eastern white pine, basswood (*Tilia*), quaking aspen, bigtooth aspen (*Populus grandidentata*), scarlet oak, chestnut oak (*Quercus prinus*), and northern red oak.

Table 7. Estimated park rankings¹ according to risk of nutrient enrichment impacts on sensitive receptors (Source: Sullivan et al. 2011a)

Park Name ²	Park Code	Estimated Nutrient N Pollutant Exposure	Estimated Ecosystem Sensitivity to Nutrient N Enrichment
Appomattox Court House	APCO	High	Low
Booker T. Washington	BOWA	Moderate	Very Low
Eisenhower	EISE	Very High	Moderate
Fredericksburg and Spotsylvania	FRSP	Very High	Low
Gettysburg	GETT	Very High	Moderate
Hopewell Furnace	HOFU	Very High	Moderate
Petersburg	PETE	Very High	Very Low
Richmond	RICH	Very High	Low
<i>Shenandoah</i>	SHEN	Very High	Very Low
Valley Forge	VAFO	Very High	High

¹ Relative park rankings are designated according to quintile ranking, among all I&M Parks, from the lowest quintile (Very Low risk) to the highest quintile (Very High risk).

² Park names are printed in bold italic for parks larger than 100 mi².

Eastern hardwood forests can respond to increased N deposition with a decrease in biodiversity of understory species (Gilliam et al. 2006a, 2006b). The response of the herbaceous layer of the forest can be pronounced, with an initial increase in herbaceous plant cover, followed by decrease in species richness and decrease in species evenness. The response time is typically shorter if ambient N deposition is relatively high (Fraterrigo et al. 2009, Gilliam et al. 2006a, 2006b, Gilliam et al. 2011, Royo et al. 2010). Because the plants in the herbaceous layer of eastern hardwood forests tend to have foliage with relatively high nutrient content, herbaceous plants influence N cycling to a level that is disproportionate to their biomass (Gilliam et al. 2011, Moore et al. 2007, Muller 2003, Welch et al. 2007). Foliar N concentration in American beech (*Fagus grandifolia*), sugar maple, and yellow birch has also been found to increase along an N deposition gradient from about 9 to 15 kg N/ha/yr across North Carolina and Virginia (Boggs et al. 2005).

Forest vegetation monitoring was conducted in 2012 at MIDN parks (Comiskey 2013). Part of the monitoring focus was on forest soil C:N ratios in the upper mineral soil. A ratio > 25 was classified as good, and represents low potential for nitrification and N saturation. A ratio < 20 was classified as indicating significant concern. Based on the samples collected in 2012, APCO, BOWA, FRSP (one site of three), GETT, PETE (one site of two), and VAFO were all rated as reflecting significant concern. The C:N was rated as good only at FRSP (one site of three) and PETE (one site of two). HOFU, VAFO, and FRSP (one site of three) had C:N between 20 and 25, and were classified as reflecting caution by Comiskey (2013)

Pardo et al. (2011b) compiled data on empirical CL for protecting sensitive resources in Level I ecoregions across the conterminous United States against nutrient enrichment effects caused by atmospheric N deposition. Available data on empirical CL of N compiled by Pardo et al. (2011b)

suggested that the lower end of the reported empirical CL range for resource protection was consistently around 3-8 kg N/ha/yr (Table 8). This applied to protection of mycorrhizal fungi, lichens, and forest vegetation and to prevent leaching of NO_3^- in drainage waters. Ambient N deposition reported by Pardo et al. (2011b) at each of the parks in the MIDN was higher than 9 kg N/ha/yr. At SHEN and VAFO, the empirical CL for protecting herbaceous plants was also exceeded. Thus, these empirical data suggest widespread exceedance of the CL for nutrient-N deposition at parks throughout the MIDN.

Table 8. Empirical critical loads for nitrogen in the MIDN, by ecoregion and receptor from Pardo et al. (2011b). Ambient N deposition reported by Pardo et al. (2011b) is compared to the lowest critical load for a receptor to identify potential exceedance, indicated by graying. A critical load exceedance suggests that the receptor is at increased risk for harmful effects.

NPS Unit	Ecoregion	N Deposition (kg N/ha/yr)	Critical Load (kg N/ha/yr)				Nitrate Leaching
			Mycorrhizal Fungi	Lichen	Herbaceous Plant	Forest	
Appomattox Court House NHP	Eastern Temperate Forests	11.9	5 - 12	4 - 8	17.5	3 - 8	8
Booker T. Washington NM	Eastern Temperate Forests	9.9	5 - 12	4 - 8	17.5	3 - 8	8
Eisenhower NHS	Eastern Temperate Forests	16.1	5 - 12	4 - 8	17.5	3 - 8	8
Fredericksburg & Spotsylvania NMP	Eastern Temperate Forests	12.6	5 - 12	4 - 8	17.5	3 - 8	8
Gettysburg NMP	Eastern Temperate Forests	16.1	5 - 12	4 - 8	17.5	3 - 8	8
Hopewell Furnace NHS	Eastern Temperate Forests	17.2	5 - 12	4 - 8	17.5	3 - 8	8
Petersburg NB	Eastern Temperate Forests	14.9	5 - 12	4 - 8	17.5	3 - 8	8
Richmond NBP	Eastern Temperate Forests	14.9	5 - 12	4 - 8	17.5	3 - 8	8
Shenandoah NP	Eastern Temperate Forests	18.8	5 - 12	4 - 8	17.5	3 - 8	8
Valley Forge NHP	Eastern Temperate Forests	17.6	5 - 12	4 - 8	17.5	3 - 8	8

There is also evidence that air pollution may have impacted lichen species distributions in the MIDN. McCune et al. (1997) found some air pollution-tolerant epiphytic lichen species, but relatively low richness of epiphytic lichen species, in urban and industrial areas within Virginia and states to the south. In rural areas, in contrast, air pollution-sensitive lichen species were more common, and richness was higher.

Ellis et al. (2013) estimated the CL for nutrient-N deposition to protect the most sensitive ecosystem receptors in 45 national parks. The lowest terrestrial CL of N is generally estimated for protection of lichens (Geiser et al. 2010). Changes to lichen communities may signal the beginning of other changes to the ecosystem that might affect structure and function (Pardo et al. 2011a). Ellis et al. (2013) estimated the N CL for SHEN in the range of 3-8 kg N/ha/yr for protection of hardwood forests(2013)(2013)(2013)(2013)(2013)(2013).

Ozone Injury to Vegetation

Ozone levels are high throughout the region in which the MIDN is located. Two of the MIDN parks, HOFU and VAFO, are in counties designated by EPA as nonattainment for the O₃ standard because of their high O₃ levels. Of all national parks where O₃ is monitored, SHEN has had among the highest measured concentrations of O₃ that can adversely affect human health and vegetation. During the period 1997 through 2001, the park's air quality did not meet EPA's O₃ standard to protect human health and welfare (Sullivan et al. 2003), but more recently O₃ levels have decreased and the area now meets the standard. Scientists have found that some sensitive plants in natural ecosystems may be injured at SUM06 levels of 8 to 12 ppm-hr (Heck and Cowling 1997). The average cumulative O₃ exposure at Big Meadows, a monitoring station in SHEN, during the late 1990s was several times higher than these suggested injury thresholds. During the 1990s, O₃ levels in SHEN generally showed an increasing trend. Over the following several years, O₃ concentrations stabilized (Sullivan et al. 2003) and subsequently declined.

The O₃-sensitive plant species that are known or thought to occur within the I&M parks found in the MIDN are listed in Table 9. Those considered to be bioindicators exhibit distinctive symptoms when injured by O₃ (e.g., dark stipple), and are designated by an asterisk. Each park within the network contains at least 16, and SHEN contains 36, O₃ sensitive and/or bioindicator species.

Ozone Exposure Indices and Levels

Kohut (2007b) assessed the risk of foliar injury from O₃ exposure during the period 1995-1999 in 10 parks in the MIDN, based on in-park monitoring of O₃ concentration in SHEN and kriging of data from surrounding monitoring stations in the other 9 parks. The SUM06 index exceeded the threshold for foliar injury in all 10 parks investigated. The W126 index exceeded the threshold in 8 parks, all except BOWA and SHEN. In SHEN, the one-hour concentration of O₃ fulfilled the W126 threshold in only two of five years evaluated. However, the O₃ concentrations in SHEN exceeded 100 ppb for a few hours during most years and for many hours during one year. It is likely that these higher exposures could injure plant foliage (Kohut 2007b). In general, in each of the parks studied, when O₃ concentration was high, soil moisture was low, thereby reducing the uptake of O₃ into foliage and its effectiveness in producing foliar injury. The probability of injury at the parks was judged to be greatest during years when O₃ levels exceeded thresholds and soil moisture was high enough so that it was unlikely that there were long-term constraints on O₃ uptake.

The W126 and SUM06 exposure indices calculated by NPS staff are given in Table 10, along with Kohut's (2007a) O₃ risk ranking. The NPS and Kohut ranking systems differ. The NPS ranking system (NPS 2010) is a quick assessment of O₃ condition that ranks O₃ exposure levels according to injury thresholds from the literature (Heck and Cowling 1997), using a 5-year average of either the W126 or SUM06 index. The former is a measure of cumulative O₃ exposure that preferentially weights higher concentrations; the latter is a measure of cumulative O₃ exposure that includes only hourly concentrations over 60 ppb. Both metrics are calculated over a 3-month period. The W126 was classified as Moderate exposure at values between 7 and 13 ppm-hr, as defined by NPS (2010). Values higher than 13 ppm-hr were classified as High exposure, and values lower than 7 ppm-hr

were classified as Low exposure. The SUM06 was classified as Moderate at values between 8 and 15 ppm-hr. Higher and lower values were classified as High and Low, respectively, as defined by NPS (2010).

Table 9. Ozone sensitive and bioindicator plant species known or thought to occur in the I&M parks of the MIDN. (Data Source: E. Porter, National Park Service, pers. comm., August 30, 2012); lists are periodically updated at <https://irma.nps.gov/NPSpecies/Report>.

Species	Common Name	Park ¹									
		APCO	BOWA	EISE	FRSP	GETT	HOFU	PETE	RICH	SHEN	VAFO
<i>Ageratina altissima</i> var. <i>altissima</i> *	White snakeroot					x					
<i>Ailanthus altissima</i> *	Tree-of-heaven	x	x	x	x	x	x	x	x	x	x
<i>Alnus incana</i> spp. <i>rugosa</i> *	Speckled alder									x	
<i>Alnus rugosa</i> *	Speckled alder						x				
<i>Apios americana</i> *	Groundnut				x		x	x	x	x	
<i>Apocynum androsaemifolium</i> *	Spreading dogbane					x	x			x	
<i>Apocynum cannabinum</i>	Dogbane, Indian hemp	x		x	x	x	x	x	x	x	x
<i>Asclepias exaltata</i> *	Tall milkweed						x			x	
<i>Asclepias incarnata</i>	Swamp milkweed			x	x	x			x	x	x
<i>Asclepias syriaca</i> *	Common milkweed	x		x	x	x	x	x	x	x	x
<i>Aster macrophyllus</i> *	Big-leaf aster						x				
<i>Cercis canadensis</i> var. <i>canadensis</i> *	Redbud							x	x		
<i>Cercis canadensis</i> *	Redbud	x	x		x	x	x			x	x
<i>Clematis virginiana</i>	Virgin's bower			x	x	x	x	x	x	x	x
<i>Corylus americana</i> *	American hazelnut		x	x	x	x	x		x	x	
<i>Eupatorium rugosum</i> *	White snakeroot						x				x
<i>Fraxinus americana</i> *	White ash	x	x	x	x	x	x	x	x	x	x
<i>Fraxinus pennsylvanica</i>	Green ash	x	x	x	x	x	x	x	x	x	x
<i>Gaylussacia baccata</i> *	Black huckleberry		x		x		x	x	x	x	x
<i>Liquidambar styraciflua</i>	Sweetgum				x			x	x		x
<i>Liriodendron tulipifera</i> *	Yellow-poplar	x	x		x	x	x	x	x	x	x
<i>Lyonia ligustrina</i> *	Maleberry				x		x		x	x	
<i>Parthenocissus quinquefolia</i>	Virginia creeper	x	x	x	x	x	x	x	x	x	x
<i>Philadelphus coronarius</i>	Sweet mock orange									x	x

¹ Park acronyms are printed in bold italic for parks larger than 100 mi².

* Bioindicator species

Table 9 (continued). Ozone sensitive and bioindicator plant species known or thought to occur in the I&M parks of the MIDN. (Data Source: E. Porter, National Park Service, pers. comm., August 30, 2012); lists are periodically updated at <https://irma.nps.gov/NPSpecies/Report>.

Species	Common Name	Park ¹									
		APCO	BOWA	EISE	FRSP	GETT	HOFU	PETE	RICH	SHEN	VAFO
<i>Pinus pungens</i>	Table-mountain pine									x	
<i>Pinus rigida</i>	Pitch pine					x	x			x	
<i>Pinus taeda</i>	Loblolly pine	x	x		x			x	x		
<i>Pinus virginiana</i>	Virginia pine	x	x		x	x	x	x	x	x	
<i>Platanus occidentalis</i> *	American sycamore	x	x	x	x	x	x	x	x	x	x
<i>Populus tremuloides</i> *	Quaking aspen					x				x	
<i>Prunus serotina</i> var. <i>serotina</i> *	Black cherry				x			x	x		
<i>Prunus serotina</i> *	Black cherry	x	x	x		x	x			x	x
<i>Prunus virginiana</i>	Choke cherry			x		x	x			x	x
<i>Rhus copallina</i>	Winged sumac	x	x				x				x
<i>Rhus copallinum</i>	Winged sumac				x			x	x	x	
<i>Robinia pseudoacacia</i>	Black locust	x	x		x	x	x	x	x	x	x
<i>Rubus allegheniensis</i> *	Allegheny blackberry	x		x	x	x	x			x	x
<i>Rubus canadensis</i> *	Thornless blackberry									x	
<i>Rudbeckia laciniata</i> *	Cutleaf coneflower			x	x	x	x			x	x
<i>Sambucus canadensis</i> *	American elder		x				x				x
<i>Sambucus nigra</i> spp. <i>canadensis</i> *	American elder	x		x		x			x		
<i>Sambucus nigra</i> *	American elder									x	
<i>Sambucus racemosa</i> *	Red elderberry									x	
<i>Sassafras albidum</i>	Sassafras	x	x		x	x	x	x	x	x	x
<i>Solidago altissima</i>	Goldenrod			x		x	x		x		x
<i>Symphoricarpos albus</i> *	Common snowberry									x	
<i>Verbesina occidentalis</i> *	Crownbeard	x						x	x	x	
<i>Vitis labrusca</i> *	Northern fox grape	x			x	x	x	x	x	x	x

¹ Park acronyms are printed in bold italic for parks larger than 100 mi².

* Bioindicator species

Table 10. Ozone assessment results for I&M parks in the MIDN based on estimated average 3-month W126 and SUM06 ozone exposure indices for the period 2005-2009 and Kohut's (2007a) ozone risk ranking for the period 1995-1999¹.

Park Name ²	Park Code	W126		Sum06		Kohut O ₃ Risk Ranking
		Value (ppm-hr)	Ranking	Value (ppm-hr)	Ranking	
Appomattox Court House	APCO	10.12	Moderate	12.83	Moderate	Moderate
Booker T. Washington	BOWA	11.27	Moderate	14.77	Moderate	Moderate
Eisenhower	EISE	12.60	Moderate	16.87	High	High
Fredericksburg and Spotsylvania	FRSP	12.01	Moderate	15.46	High	High
Gettysburg	GETT	12.70	Moderate	16.95	High	High
Hopewell Furnace	HOFU	14.12	High	18.73	High	High
Petersburg	PETE	13.02	High	17.02	High	Moderate
Richmond	RICH	13.66	High	17.80	High	Moderate
<i>Shenandoah</i>	SHEN	10.05	Moderate	12.88	Moderate	Moderate
Valley Forge	VAFO	14.48	High	19.13	High	High

¹ Parks are classified into one of three ranks (Low, Moderate, High), based on comparison with other I&M parks.

² Park names are printed in bold italic for parks larger than 100 mi².

Kohut's approach constitutes a more rigorous assessment of potential risk to plants. It considers both O₃ exposure and environmental conditions (soil moisture). Kohut also used injury thresholds from the literature, but evaluated a different O₃ metric (after Lefohn et al. 1997), the W126 over a 5-month period in conjunction with the N100 (number of hours over 100 ppb O₃). The rationale for the N100 statistic is that higher O₃ concentrations are most likely to cause plant injury. Kohut examined five individual years of O₃ exposure and soil moisture data and considered the effects of low soil moisture on O₃ uptake each year when assigning risk. Soil moisture is important because dry conditions induce stomatal closure in plants, which has the effect of limiting O₃ uptake and injury. In areas where low soil moisture levels correspond with high O₃ exposure, uptake and injury are limited by stomatal closure even when exposures are relatively high. Ozone condition, as rated by NPS, ranges from Moderate to High in the MIDN parks. Kohut's evaluation of risk to plants also ranged from Moderate to High.

The results of both ranking systems should be considered when evaluating the potential for O₃ injury to park vegetation. The Kohut approach considered environmental conditions that significantly affect plant response to O₃, but exposures have likely changed since the time of the assessment. The NPS approach considers more recent O₃ conditions, but not environmental conditions.

Ozone Formation

Ozone formation is governed by atmospheric levels of both NO_x and volatile organic compounds (VOCs). Some information is available regarding the relative importance of these two O₃ precursors

in the MIDN, but only for one park (SHEN). The most abundant VOC compound measured in the air during summer in SHEN during the period 1995-1997 was isoprene, a natural biogenic compound (Kang et al. 2001). Upon conversion of all VOCs into propylene-equivalent concentration units (to assess relative potential contribution of VOCs to O₃ formation), biogenic components accounted for more than two-thirds of the total atmospheric VOC concentration during all three study years. About 80% of the biogenic VOC was comprised of isoprene; other common VOCs included α -pinene, β -pinene, and limonene. The major anthropogenic VOCs during summer were isopentane, toluene, and propane. These are derived from automobile exhaust (isopentane), solvents (toluene), and natural gas (propane; Kang et al. 2001).

Kang et al. (2003) applied the Multiscale Air Quality Simulation Platform (MAQSIP) model to predict atmospheric O₃ concentration in SHEN and two other parks. Modeling results suggested that VOCs were chemically saturated, potentially causing decreased O₃ production in response to further increases in VOC emissions. More than half of the O₃ at SHEN was simulated to be transported from other areas (Kang et al. 2003). The authors concluded that, in areas like SHEN where transport from pollutant source areas dominates the local O₃ production, a control strategy might focus on reduction of O₃ in the source region(s).

Ozone Exposure Effects

Ground-level O₃ constitutes a stress to O₃-sensitive vegetation in SHEN that can interact with other, potentially exacerbating stresses such as drought, insects, and diseases. Ozone also causes visible foliar symptoms on several plant species in SHEN, including but not limited to milkweed (*Asclepias* spp.), black cherry, yellow poplar, and white ash (*Fraxinus Americana*; Chappelka et al. 1999, Sullivan et al. 2003). However, little is known about the relationship between visible foliar symptoms and the growth or vitality of sensitive plant species.

Foliar injury due to O₃ exposure was documented by Chappelka et al. (1999) on mature black cherry in GRSM and SHEN. Trees growing at the highest elevations in both parks showed the most severe symptoms during all three years of study. These high-elevation sites also received the highest O₃ exposures. The percent of trees injured by O₃ was positively correlated with both the SUM06 and W126 indices.

Responses of eight tree species to the isolated effects of O₃ exposures were simulated by Sullivan et al. (2003) using the TREGRO model, and ranked in order from most to least sensitive to growth and species composition impacts:

White ash>Basswood=Chestnut oak>Red maple>Yellow poplar>Black cherry=Red oak>Sugar maple.

Simulations suggested that white ash is more sensitive to growth and species composition impacts than other tree species in SHEN, both as an individual and as a component of a forest stand. Ambient O₃ exposure caused an estimated 1% decrease in total growth of white ash, a long-lived species, over the three year simulation period. Over a 100-year simulation period, projected 1997 through 1999 ambient O₃ exposures were expected to cause a 50% decrease in white ash species composition in

chestnut oak forests. Ground-level O₃ exposures greater than ambient levels were projected to cause a less than 10% decrease in white ash and yellow poplar species composition in cove hardwood forests over 100 years. Modeling results suggested that O₃ exposures about 15% less than 1997 through 1999 ambient levels should protect against isolated changes in white ash growth and species composition in the park's forests.

Field plots and open-top chambers were established in Big Meadows in SHEN in 1979 to investigate the effects of O₃ on tree seedlings. Studies conducted from 1979 to 1981 suggested that ambient levels of O₃ caused foliar injury on seedlings of yellow poplar, green ash (*Fraxinus pennsylvanica*), and sweetgum (*Liquidambar styraciflua*), as well as reduced average height growth of yellow poplar, green ash, black locust (*Robinia pseudoacacia*), Virginia pine (*Pinus virginiana*), eastern white pine, table mountain pine, (*Pinus pungens*), and eastern hemlock (Duchelle et al. 1982). It must be recognized, however, that open-top chambers might enhance height growth due to reduced wind stress, so the results of such experiments may not necessarily reflect O₃ exposure effects in the field. A concurrent study found that ambient O₃ concentrations reduced above-ground biomass production of native vegetation compared to charcoal-filtered air (Duchelle et al. 1983).

Foliar injury surveys were conducted on five native plant species in SHEN in 1982. Three of the five species (virgin's bower [*Clematis virginiana*], black locust, and wild grape [*Vitis* sp.]) displayed increased injury with increased elevation (Winner et al. 1989). In 1991, trend plots of the O₃-sensitive hardwoods yellow poplar, black cherry, and white ash were established near the ambient O₃ monitors at Dickey Ridge, Big Meadows, and Sawmill Run in the park. Marked trees in each plot were evaluated for foliar O₃ injury in 1991, 1992, and 1993 (Hildebrand et al. 1996). Black cherry and white ash exhibited increased foliar symptoms with increased O₃ exposure across all three sites and at each site across all years of study. Whereas the amount of foliar symptoms on yellow poplar at Dickey Ridge corresponded well with O₃ exposure, there was no correlation for this species at the Big Meadows or Sawmill Run sites. The authors speculated the lack of correlation for yellow poplar at Big Meadows and Sawmill Run may have been due to extremes in moisture availability at the two sites. Hildebrand et al. (1996) concluded that cumulative O₃ statistics, such as SUM06 and W126, best represented foliar injury observations, particularly for black cherry, during the period of study.

Visibility Degradation

Natural Background and Ambient Visibility Conditions

The Clean Air Act set a specific goal for visibility protection in Class I areas: “the prevention of any future, and the remedying of any existing, impairment of visibility¹ in mandatory Class I federal areas which impairment results from manmade air pollution” (42 U.S.C. 7491). In 1999, EPA passed the Regional Haze Rule (RHR), which requires each state to develop a plan to improve visibility in Class I areas, with the goal of returning visibility to natural conditions in 2064. Visibility is monitored by the Interagency Monitoring of Protected Visual Environments (IMPROVE) Network and typically reported using the haze index deciview² (dv).

Visibility is currently degraded throughout SHEN, the one Class I park in the MIDN, detracting from visitor enjoyment of scenic vistas. This is especially problematic along Skyline Drive, which is designated a Virginia State Scenic Highway. These scenic vistas are also enjoyed by visitors hiking the Appalachian National Scenic Trail through the park. Sullivan et al. (2003) concluded that the ambient annual average visual range (VR) was only about 20 percent of the estimated natural VR of about 115 miles (185 km). Even the mean of the clearest 20 percent of days, which occur mostly in winter, are degraded by human-made particles in the air in SHEN.

Within the MIDN, there is an IMPROVE site at SHEN. Natural background and ambient visibility conditions have been estimated for SHEN for the 20% clearest visibility days, the 20% haziest visibility days, and average days. Data are also available that are considered to be representative of visibility conditions in four Class II areas (APCO, EISE, FRSP, and GETT), based on measured values taken from IMPROVE sites in the region. EPA considers an IMPROVE monitor to be representative of an area if it is located within 60 mi (100 km) and 425 ft (130 m) elevation of the area. Natural background visibility, the goal of the Clean Air Act, assumes no human-caused pollution, but varies with natural processes such as windblown dust, fire, volcanic activity and biogenic emissions.

Current visibility estimates reflect current pollution levels and were used to rank conditions at parks in order to provide park managers with information on spatial differences in visibility and air pollution. Rankings range from very low haze (very good visibility) to very high haze (very poor visibility). Only parks with on-site or representative data from IMPROVE monitors were used in

¹ Visibility impairment means any humanly perceptible change in visibility (light extinction, visual range, contrast, coloration) from that which would have existed under natural conditions.

² The *deciview* visibility metric expresses uniform changes in haziness in terms of common increments across the entire range of visibility conditions, from pristine to extremely hazy conditions. Because each unit change in deciview represents a common change in perception, the deciview scale is like the decibel scale for sound. A one deciview change in haziness is a small but noticeable change in haziness under most circumstances when viewing scenes in Class I areas.

generating the baseline visibility ranking. Table 11 gives the relative park haze rankings on the 20% clearest, 20% haziest, and average days. Haze was generally Very High at all parks in the MIDN.

Annual mean dv levels on the haziest days at 47 monitored park locations during the period 2006-2008 ranged from 1.5 to 21 dv higher than the estimated natural condition (NPS 2010). The average difference between measured dv and estimated natural condition was 8.3 dv. Several eastern parks had annual mean dv on the haziest days that were substantially higher (more than about 10 dv) than estimated natural conditions; these included the MIDN parks with on-site or representative monitoring. Monitoring sites showing the largest differences during the period 2006-2008 between measured visibility and estimated natural conditions on the clearest days also included SHEN (NPS 2010). On average days during the period 2004-2008, ambient haze at SHEN was nearly 22 dv higher than the estimated average natural haze and more than about 12-15 dv higher at several other MIDN parks (APCO, EISE, FRSP, GETT; Table 11).

Representative photos of a selected vista in SHEN under three different visibility conditions are shown in Figure 6. Photos were selected to correspond with the clearest 20% of visibility conditions, haziest 20% of visibility conditions, and annual average visibility conditions at that location. This series of photos provides a graphic illustration of the visual effect of these differences in haze level in this park.

IMPROVE data allow us to estimate VR. Data from Arendtsville, PA (representative of EISE and GETT) indicate that pollution at that site has reduced average VR from 110 miles to 20 miles (177 to 32 km). On the haziest days, VR has been reduced from 70 to 10 miles (113 to 16 km). Severe haze episodes occasionally reduce visibility to 5 miles (8 km). At James River Face Wilderness (representative of APCO), pollution has reduced average VR from 110 miles to 25 miles (177 to 40 km). On the haziest days, VR has been reduced from 80 to 15 miles (129 to 24 km). Severe haze episodes occasionally reduce visibility to 6 miles (10 km). At the Washington DC site (representative of FRSP) pollution has reduced average VR from 100 to 20 miles (161 to 32 km). On the haziest days, VR has been reduced from 75 to 10 miles (121 to 16 km). Severe haze episodes occasionally reduce visibility to 6 miles (10 km). At SHEN, air pollution has reduced average VR from 120 to 25 miles (193 to 40 km). On the haziest days, VR has been reduced from 75 to 10 miles (121 to 16 km). Severe haze episodes occasionally reduce visibility to 5 miles (8 km).

Composition of Haze

Various pollutants make up the haze that causes visibility degradation. IMPROVE measures these pollutants and reports them as ammonium sulfate ((NH₄)₂SO₄), ammonium nitrate, elemental carbon, coarse mass, organic mass, sea salt, and soil. Sulfates form in the atmosphere from sulfur dioxide emissions from coal-burning power plants, smelters, and other industrial facilities. Nitrates form in the atmosphere from NO_x emissions from combustion sources including vehicles, power plants, industry, and fires. Organic compounds are emitted from a variety of both natural (biogenic) and human-caused sources, including agriculture, industry, and fires. Atmospheric sea salt concentrations are higher in coastal areas. Soil can enter the atmosphere through both natural processes and human disturbance.

Figure 7 shows estimated natural (pre-industrial), baseline (2000-2004), and current (2006-2010) levels of haze and its composition for APCO, EISE, FRSP, GETT, and SHEN. The figure illustrates that SO_4^{2-} is the primary component of ambient haze at all five parks on the 20% clearest, annual average, and 20% haziest visibility days. Organics and nitrates also contribute significantly to ambient haze at these parks. Under estimated natural conditions, in the absence of anthropogenic air pollution, organics dominated the extinction budget.

In SHEN, the majority of total particulate light extinction (b_{ext}) was attributable to SO_4^- (Figure 7). On an annual average basis, 70.73% of total particulate light extinction (b_{ext}) was attributable to SO_4^- , while 8.98% was contributed by NO_3^- , and 11.39% was from organics. On the 20% haziest days, b_{ext} was mostly comprised of SO_4^{2-} extinction, which accounted for 80.71% of b_{ext} ; NO_3^- contributed only 2.86%, and organics contributed 10.28%. On the 20% clearest visibility days, the SO_4^{2-} contribution decreased to 55.12% while NO_3^- and organics both increased to 17.73% and 12.40% of b_{ext} , respectively.

Trends in Visibility

Changes in visibility over time in the MIDN are mainly caused by changes in the concentration of particles of $(\text{NH}_4)_2\text{SO}_4$ in the atmosphere. Atmospheric $(\text{NH}_4)_2\text{SO}_4$ is primarily derived from human sources of air pollution. Sullivan et al. (2003) concluded that seasonal variability in the mean of the haziest 20% fractions in SHEN was driven primarily by $(\text{NH}_4)_2\text{SO}_4$ extinctions.

NPS (2010) reported long-term trends in annual deciview on the clearest and haziest 20% of days at monitoring sites in 29 national parks. All 27 parks that showed statistically significant ($p \leq 0.05$) deciview trends on the clearest days for the 11-20 year monitoring periods through 2008 exhibited decreases in deciview over time. None of the sites showed increasing trends on the clearest days. The steepest declines (-0.18 to -0.20 dv/yr) on the clearest days were reported for SHEN, ACAD, and Washington DC, with 18-19 years of monitoring data at each of those locations. Ten parks showed statistically significant decreases in dv on the haziest days, with the second steepest decline reported for SHEN (-0.27 dv/yr).

Available monitoring data shown in Figure 8 suggest improvements in recent years on the 20% haziest, 20% clearest, and annual average days. Improvements have been most pronounced on the haziest days.

Table 11. Estimated natural background visibility (top panel) and ambient visibility conditions in MIDN parks averaged over the period 2004 through 2008 (bottom panel)¹. Representative IMPROVE sites include JARI1 in the James Face Wilderness, VA; AREN1 in Arendtsville, PA; WASH1 in Washington, DC.

Park Name ²	Park Code	Site ID	Estimated Natural Haze					
			20% Clearest Days		Average Days	20% Haziest Days		
			dv		dv			
Appomattox Court House ³	APCO	JARI1	4.39		7.55		11.13	
Booker T. Washington	BOWA	No Site						
Eisenhower ³	EISE	AREN1	4.24		7.68		11.77	
Fredericksburg and Spotsylvania ³	FRSP	WASH1	5.51		8.26		11.86	
Gettysburg ³	GETT	AREN1	4.24		7.68		11.77	
Hopewell Furnace	HOFU	No Site						
Petersburg	PETE	No Site						
Richmond	RICH	No Site						
<i>Shenandoah</i>	SHEN	SHEN1	3.14		6.90		11.35	
Valley Forge	VAFO	No Site						
Park Name	Park Code	Site ID	Measured Ambient Haze (For Years 2004 through 2008)					
			20% Clearest Days		Average Days		20% Haziest Days	
			dv	Ranking	dv	Ranking	dv	Ranking
Appomattox Court House ³	APCO	JARI1	14.06	Very High	20.94	Very High	28.35	Very High
Booker T. Washington	BOWA	No Site						
Eisenhower ³	EISE	AREN1	13.48	Very High	21.41	Very High	29.46	Very High
Fredericksburg and Spotsylvania ³	FRSP	WASH1	16.86	Very High	23.11	Very High	29.70	Very High
Gettysburg ³	GETT	AREN1	13.48	Very High	21.41	Very High	29.46	Very High
Hopewell Furnace	HOFU	No Site						
Petersburg	PETE	No Site	3.38	Low	11.08	Very Low	6.82	Very Low
Richmond	RICH	No Site						
<i>Shenandoah</i>	SHEN	SHEN1	9.95	High	28.76	Very High	18.92	Very High
Valley Forge	VAFO	No Site						

¹ Parks are classified into one of five haze ranks (Very Low, Low, Moderate, High, or Very High haze).

² Park names are printed in bold italic for parks larger than 100 mi².

³ Data are borrowed from a nearby site for APCO, EISE, FRSP, and GETT. A monitoring site is considered by IMPROVE to be representative of an area if it is within 60 mi (100 km) and 425 ft (130 m) in elevation of that area.

Shenandoah

Clearest Days

Taken: 3:00 PM

Haze = 9 dv

$B_{\text{ext}} = 24 \text{ Mm}^{-1}$

VR = 160 km



Haziest Days

Taken = 3:00 PM

Haze = 28 dv

$B_{\text{ext}} = 156 \text{ Mm}^{-1}$

VR = 25 km



Average Days

Taken = 3:00 PM

Haze = 18 dv

$B_{\text{ext}} = 60 \text{ Mm}^{-1}$

VR = 65 km



Figure 6. Three representative photos of the same view in SHEN illustrating the 20% clearest visibility, the 20% haziest visibility, and the annual average visibility. B_{ext} is total particulate light extinction; VR is visual range.

APCO (data from JARI1)

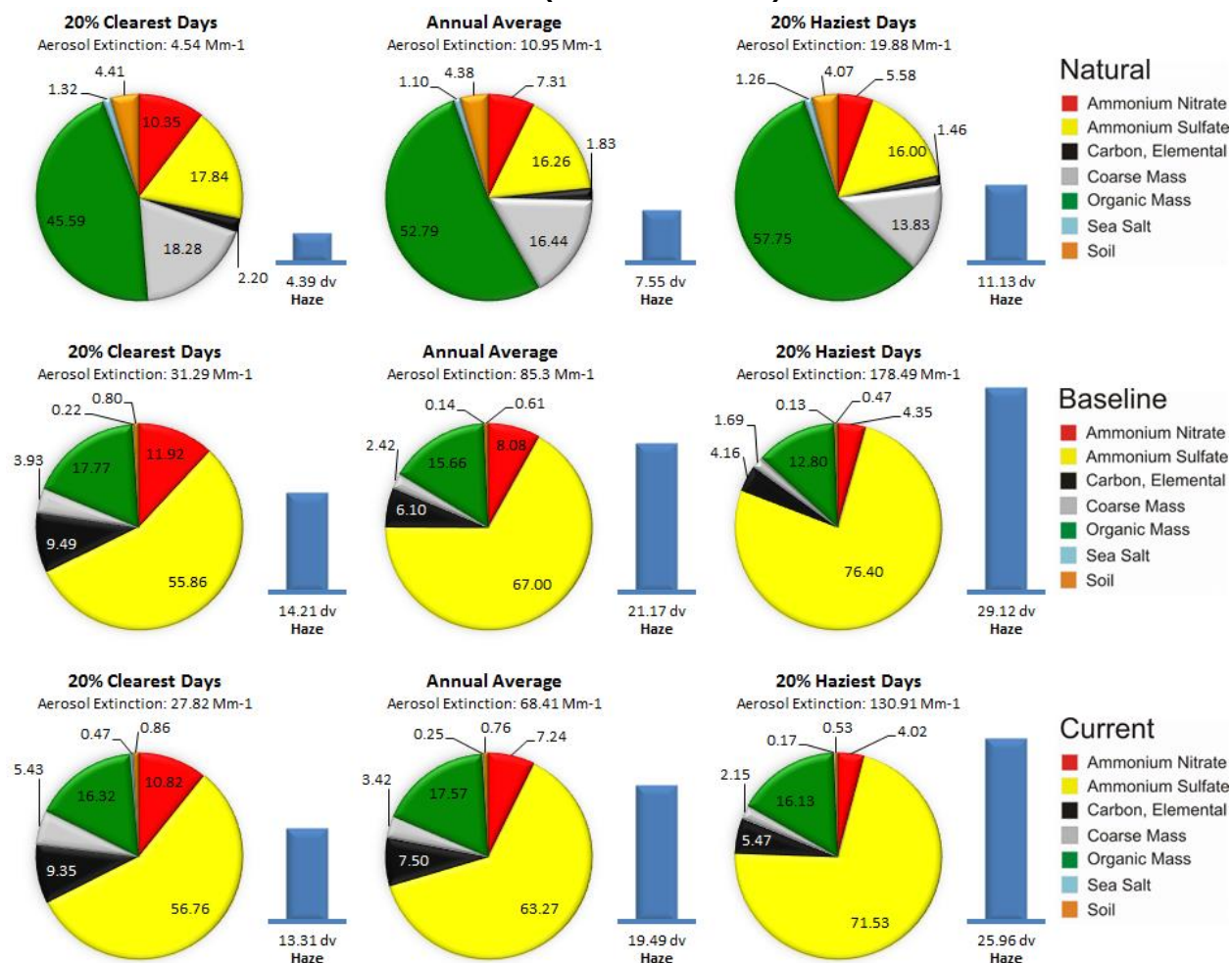


Figure 7a. Estimated natural (pre-industrial), baseline (2000-2004), and current (2006-2010) levels of haze (blue columns) and its composition (pie charts) on the 20% clearest, annual average, and 20% haziest visibility days for APCO, EISE, FRSP, GETT, PETE, and SHEN. Data for APCO, EISE, FRSP, and GETT were taken from nearby sites (see Table 11). EISE and GETT have no data for the years 2000 and 2001; APCO has no data for the year 2000; FRSP has no data for the year 2010; and PETE only has data for the years 2005-2008. Data Source: NPS-ARD.

EISE, GETT (data from AREN1)

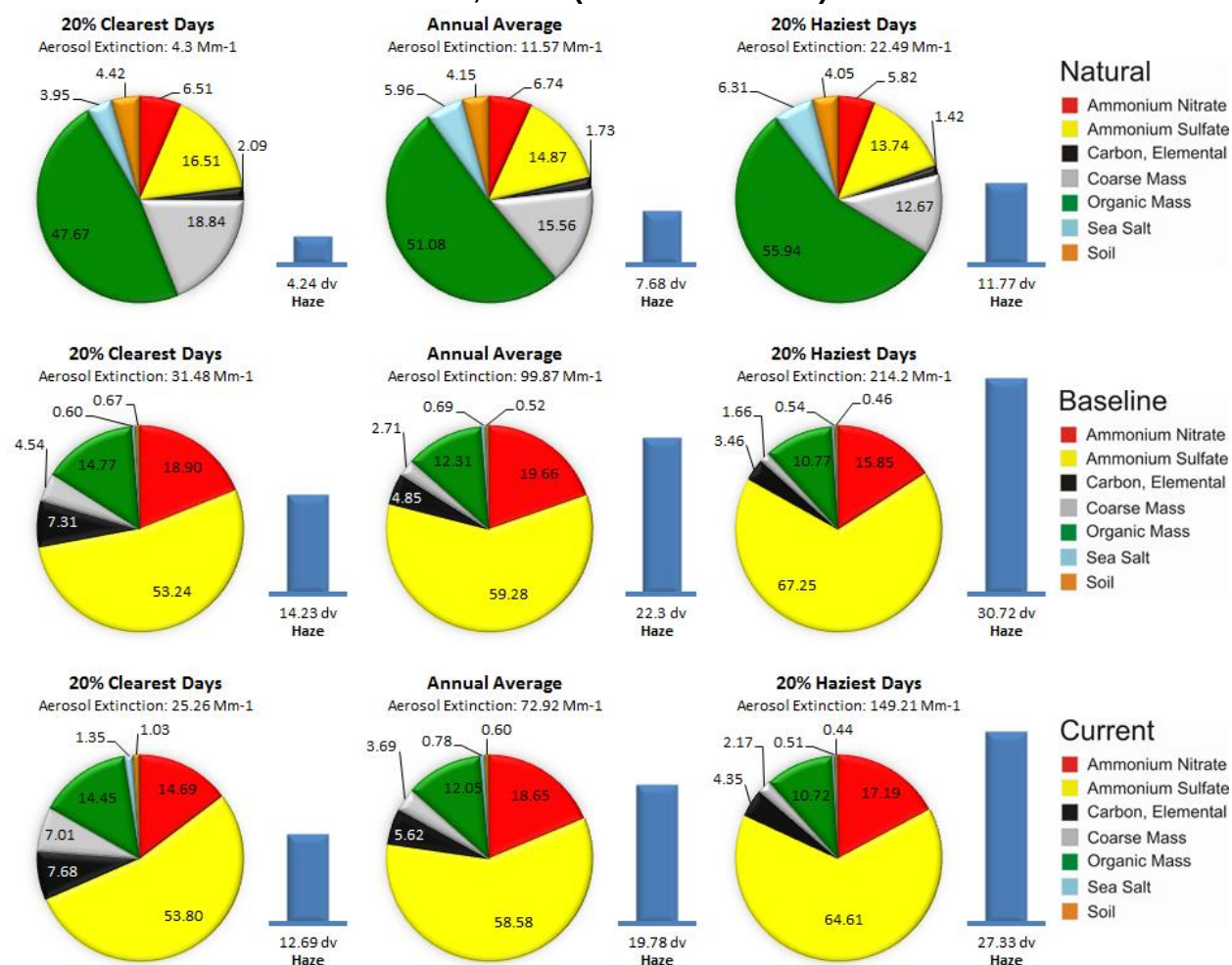


Figure 7b. Estimated natural (pre-industrial), baseline (2000-2004), and current (2006-2010) levels of haze (blue columns) and its composition (pie charts) on the 20% clearest, annual average, and 20% haziest visibility days for APCO, EISE, FRSP, GETT, PETE, and SHEN. Data for APCO, EISE, FRSP, and GETT were taken from nearby sites (see Table 11). EISE and GETT have no data for the years 2000 and 2001; APCO has no data for the year 2000; FRSP has no data for the year 2010; and PETE only has data for the years 2005-2008. Data Source: NPS-ARD.

FRSP (data from WASH1)

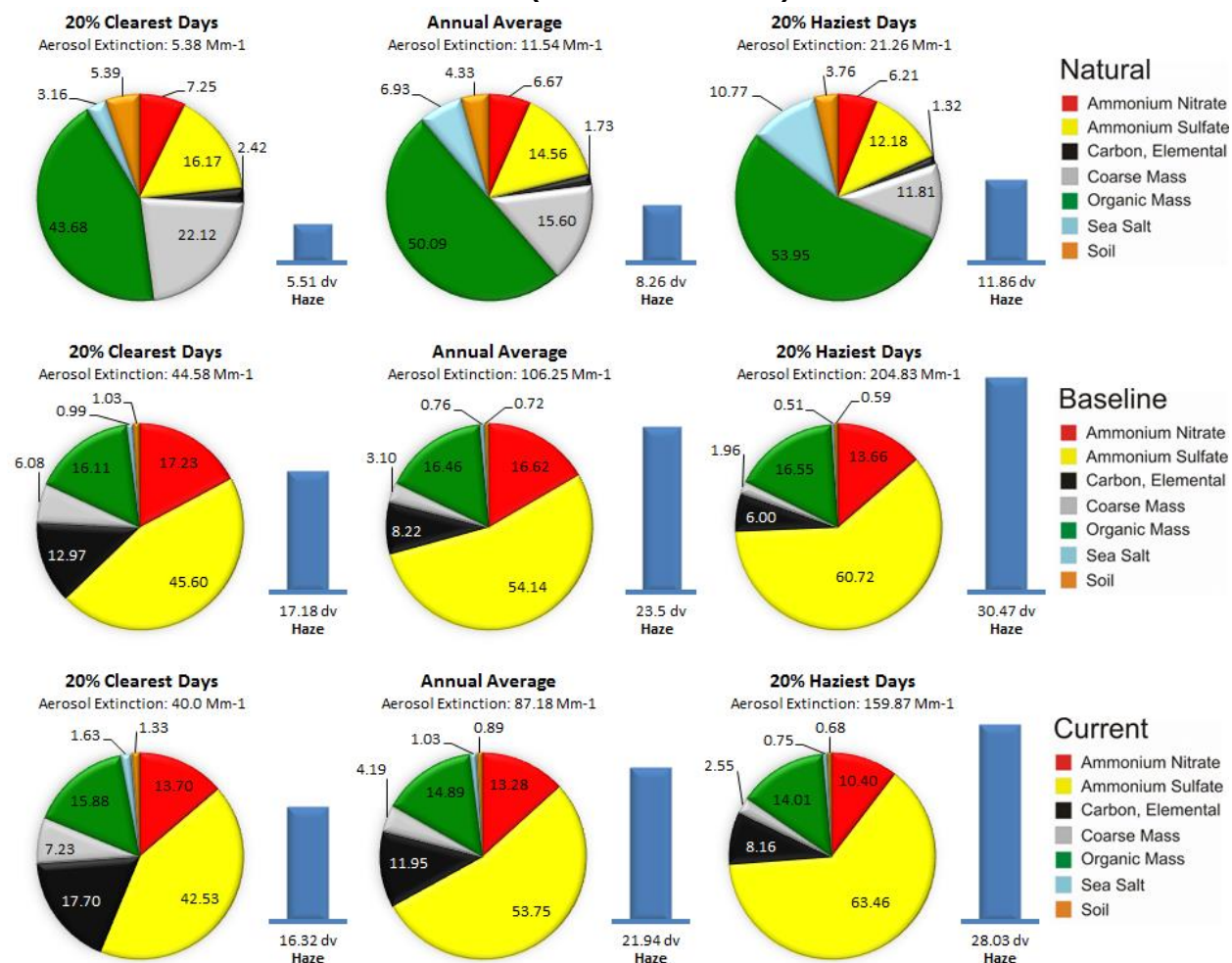


Figure 7c. Estimated natural (pre-industrial), baseline (2000-2004), and current (2006-2010) levels of haze (blue columns) and its composition (pie charts) on the 20% clearest, annual average, and 20% haziest visibility days for APCO, EISE, FRSP, GETT, PETE, and SHEN. Data for APCO, EISE, FRSP, and GETT were taken from nearby sites (see Table 11). EISE and GETT have no data for the years 2000 and 2001; APCO has no data for the year 2000; FRSP has no data for the year 2010; and PETE only has data for the years 2005-2008. Data Source: NPS-ARD.

SHEN

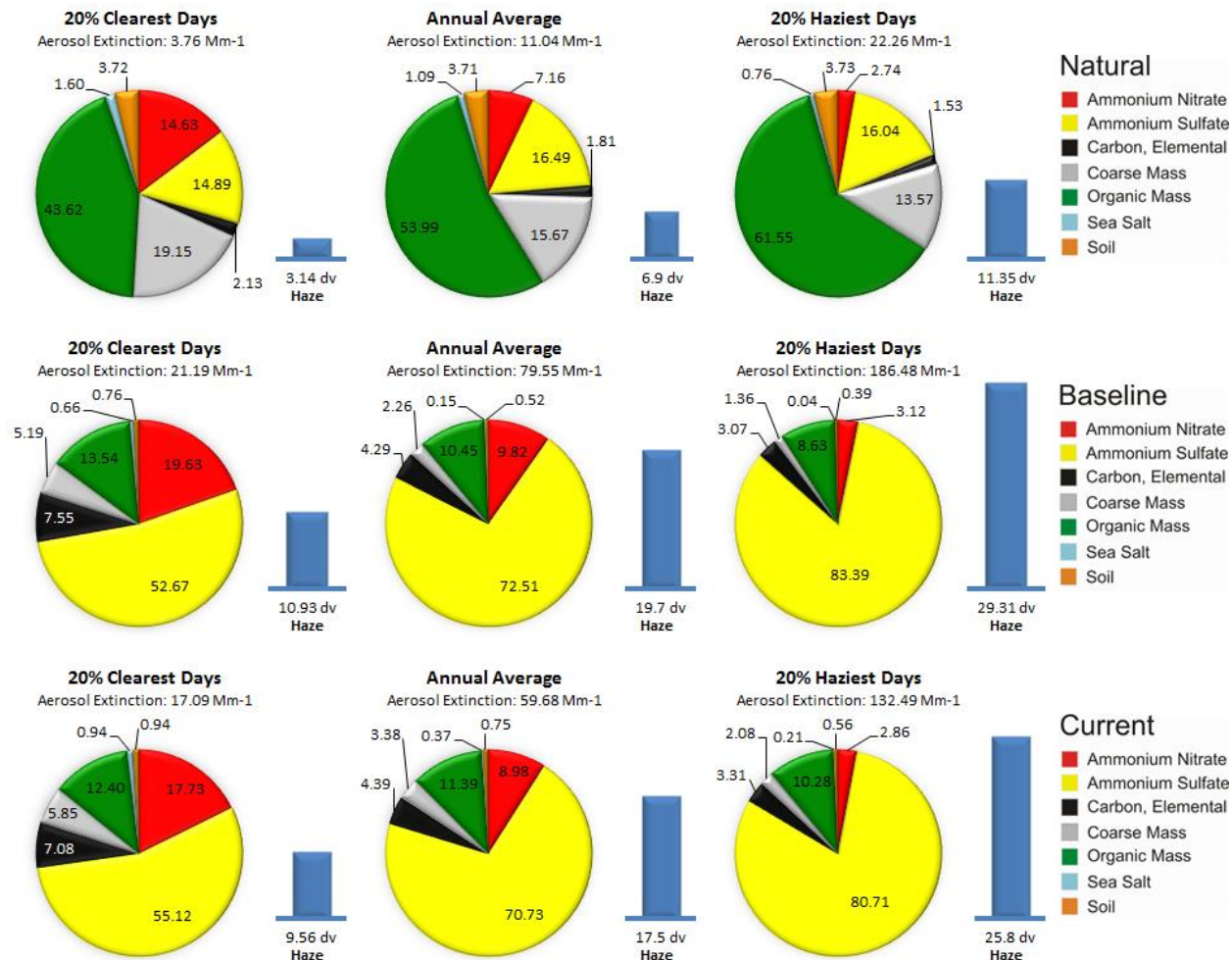


Figure 7d. Estimated natural (pre-industrial), baseline (2000-2004), and current (2006-2010) levels of haze (blue columns) and its composition (pie charts) on the 20% clearest, annual average, and 20% haziest visibility days for APCO, EISE, FRSP, GETT, PETE, and SHEN. Data for APCO, EISE, FRSP, and GETT were taken from nearby sites (see Table 11). EISE and GETT have no data for the years 2000 and 2001; APCO has no data for the year 2000; FRSP has no data for the year 2010; and PETE only has data for the years 2005-2008. Data Source: NPS-ARD.

Development of State Implementation Plans

The Visibility Improvement State and Tribal Association of the Southeast (VISTAS) is a collaborative effort among state governments, tribal governments, and federal agencies involved in management of visibility and regional haze in the Southeast. The VISTAS region includes the southeastern United States from Virginia and West Virginia in the north, south to Florida, and west to Kentucky, Tennessee, and Mississippi. According to the RHR, states and tribes must establish and meet reasonable progress goals for each federal Class I area to improve visibility on the 20% haziest days and to prevent visibility degradation on the 20% clearest days. The national goal is to return visibility in Class I areas to natural background levels in 2064. States must evaluate progress by 2018 (and every 10 years thereafter) based on a baseline period of 2000 to 2004 (Air Resource Specialists 2007).

Analyses conducted on behalf of VISTAS have included determination of baseline visibility conditions, calculation of the glideslope from the baseline necessary to achieve background conditions in 2064, and determination of air pollutant source areas. The glideslope analysis depicted in Figure 9 shows that recent improvements in visibility on the haziest days are generally following a trajectory in compliance with the RHR requirement for attaining natural visibility conditions in 2064.

Toxic Airborne Contaminants

Despite receiving relatively high levels of wet Hg deposition, SHEN has not been the subject of studies to ascertain possible biomagnification and effects of Hg or other toxic agents on fish or wildlife. Nevertheless, some information is available on the concentrations of Hg in amphibians in the MIDN. Bank et al. (2005) reported concentrations of total and MeHg in northern two-lined salamanders (*Eurycea bislineata bislineata*) collected from streams in several locations, including within SHEN. Total Hg levels in salamander larvae were significantly higher at sites in Maine, as compared with sites in SHEN. Study results suggested that watershed features, including fire, Pesticides used at the park units were judged to be generally of low toxicity, posing little or no threat to terrestrial vertebrates. Atmospheric deposition of toxic material from sources outside the park units was not assessed. Based on the estimated level of contaminant threat and the availability and quality of ecotoxicological data, Rattner and Ackerson (2006) ranked SHEN, RICH, VAFO, and HOFU as highest priority within the study region for research and monitoring on the topic of terrestrial vertebrate ecotoxicology.

Brasso and Cristol (2008) established an experimental tree swallow (*Tachycineta bicolor*) population in the headwaters of the Shenandoah River, Virginia, adjacent to a point source of Hg. Swallows nesting in the contaminated area produced fewer fledglings than those in reference areas. However, the effects of Hg were detectable only for young females that were breeding for the first time, and the relative importance of atmospheric sources of Hg was not evaluated. $(\text{NH}_4)_2\text{SO}_4$ addition, wetland extent, and forest cover type affected Hg bioaccumulation in salamanders (Bank et al. 2005).

Rattner and Ackerson (2006) conducted a study of ecotoxicological threats to 23 I&M parks units in the National Capital Region and Mid-Atlantic networks. Information was provided on existing or potential toxic pollution hazards in order to prioritize future contaminant biomonitoring activities.

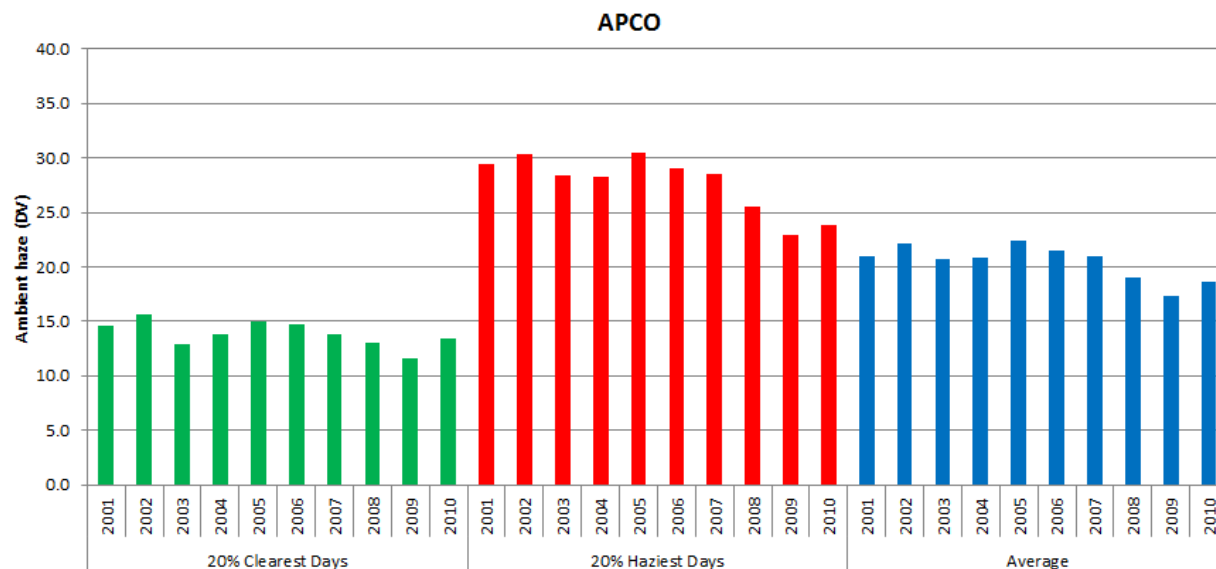


Figure 8a. Trends in ambient haze levels at APCO, based on IMPROVE measurements on the 20% clearest, 20% haziest, and annual average visibility days over the monitoring period of record. Data for APCO, EISE, FRSP, and GETT were taken from nearby sites (see Table 11). Data Source: http://vista.cira.colostate.edu/improve/Data/IMPROVE/summary_data.htm

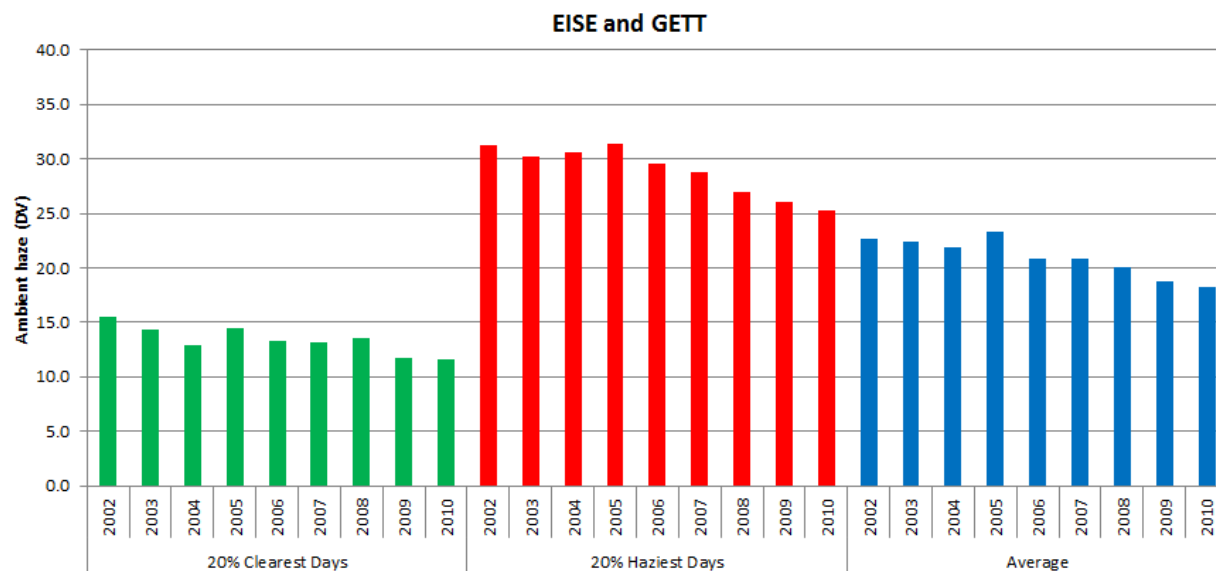


Figure 8b. Trends in ambient haze levels at EISE and GETT, based on IMPROVE measurements on the 20% clearest, 20% haziest, and annual average visibility days over the monitoring period of record. Data for APCO, EISE, FRSP, and GETT were taken from nearby sites (see Table 11). Data Source: http://vista.cira.colostate.edu/improve/Data/IMPROVE/summary_data.htm

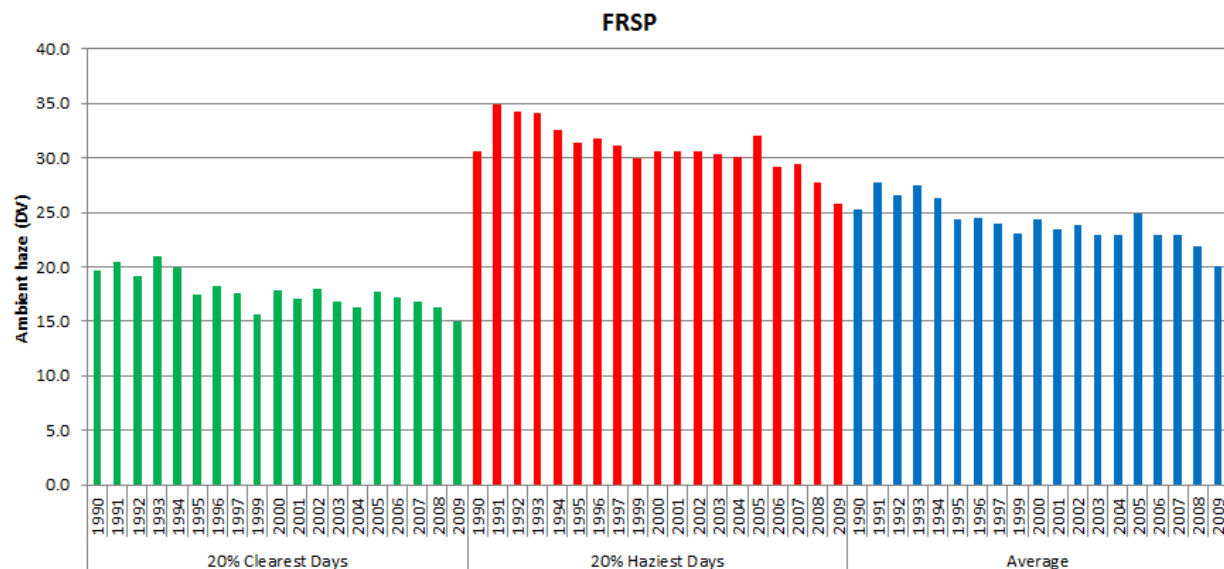


Figure 8c. Trends in ambient haze levels at FRSP, based on IMPROVE measurements on the 20% clearest, 20% haziest, and annual average visibility days over the monitoring period of record. Data for APCO, EISE, FRSP, and GETT were taken from nearby sites (see Table 11). Data Source: http://vista.cira.colostate.edu/improve/Data/IMPROVE/summary_data.htm

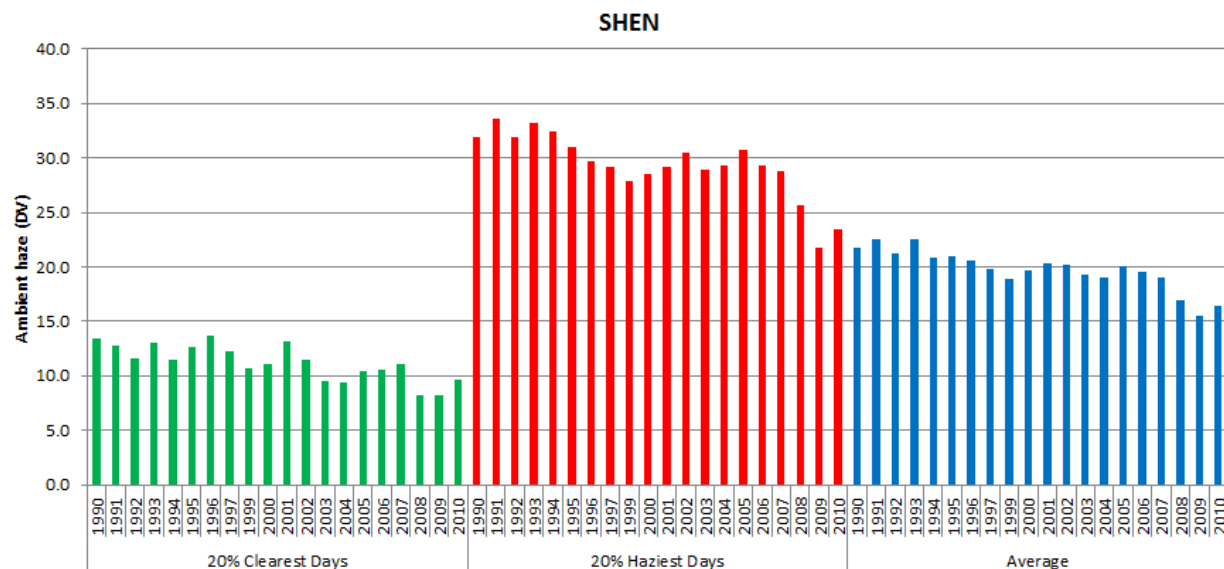


Figure 8d. Trends in ambient haze levels at SHEN, based on IMPROVE measurements on the 20% clearest, 20% haziest, and annual average visibility days over the monitoring period of record. Data for APCO, EISE, FRSP, and GETT were taken from nearby sites (see Table 11). Data Source: http://vista.cira.colostate.edu/improve/Data/IMPROVE/summary_data.htm

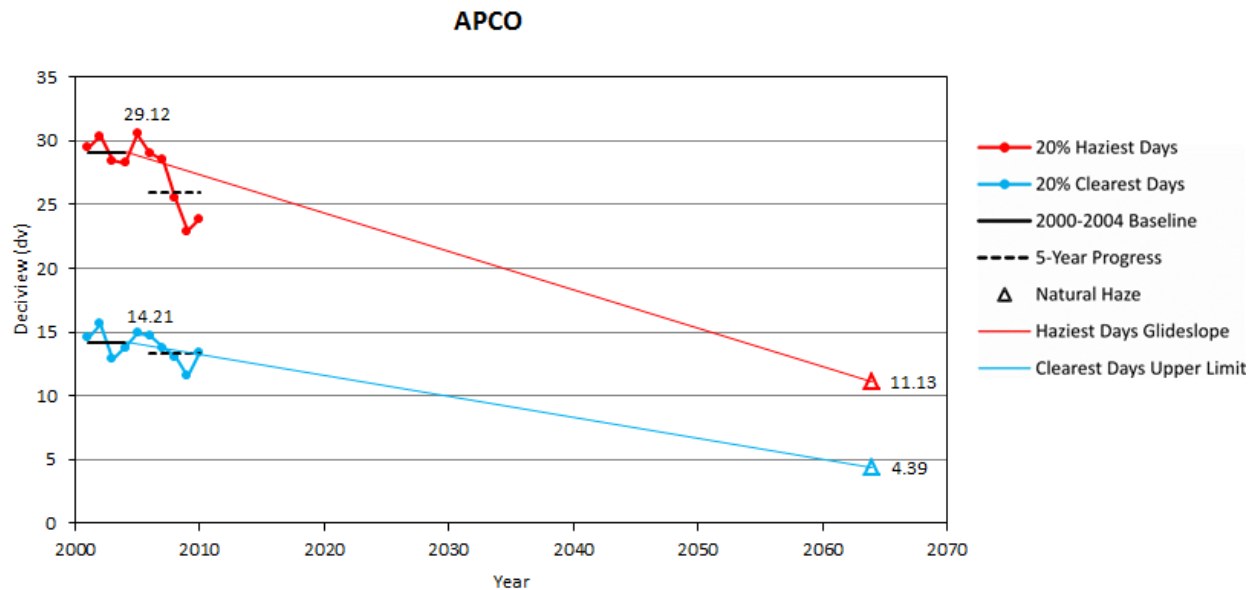


Figure 9a. Glideslopes to achieving natural visibility conditions in 2064 for the 20% haziest (red line) and the 20% clearest (blue line) days in APCO. In the regional haze rule, the clearest days do not have a uniform rate of progress glideslope; the rule only requires that the clearest days do not get any worse than the baseline period. Also shown are measured values during the period 2000 to 2010. Data for APCO, EISE, FRSP, and GETT were taken from nearby sites (see Table 11). EISE and GETT have no data for the years 2000 and 2001; APCO has no data for the year 2000; and FRSP has no data for the year 2010. Data Source: http://vista.cira.colostate.edu/improve/Data/IMPROVE/summary_data.htm

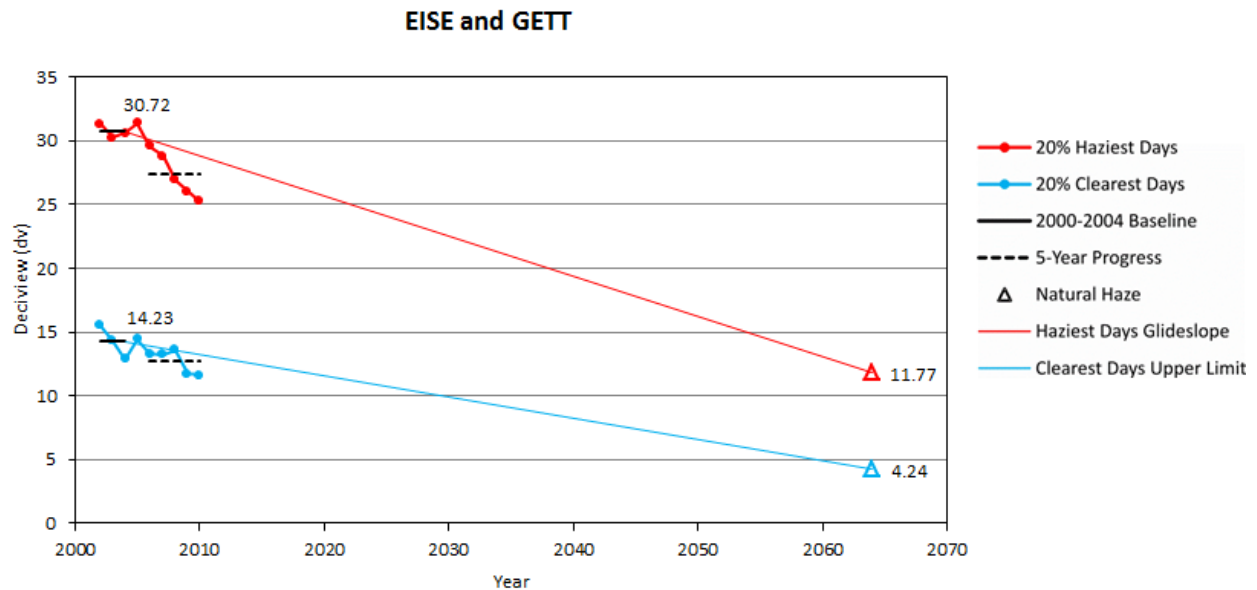


Figure 9b. Glideslopes to achieving natural visibility conditions in 2064 for the 20% haziest (red line) and the 20% clearest (blue line) days in EISE and GETT. In the regional haze rule, the clearest days do not have a uniform rate of progress glideslope; the rule only requires that the clearest days do not get any worse than the baseline period. Also shown are measured values during the period 2000 to 2010. Data for APCO, EISE, FRSP, and GETT were taken from nearby sites (see Table 11). EISE and GETT have no data for the years 2000 and 2001; APCO has no data for the year 2000; and FRSP has no data for the year 2010. Data Source: http://vista.cira.colostate.edu/improve/Data/IMPROVE/summary_data.htm

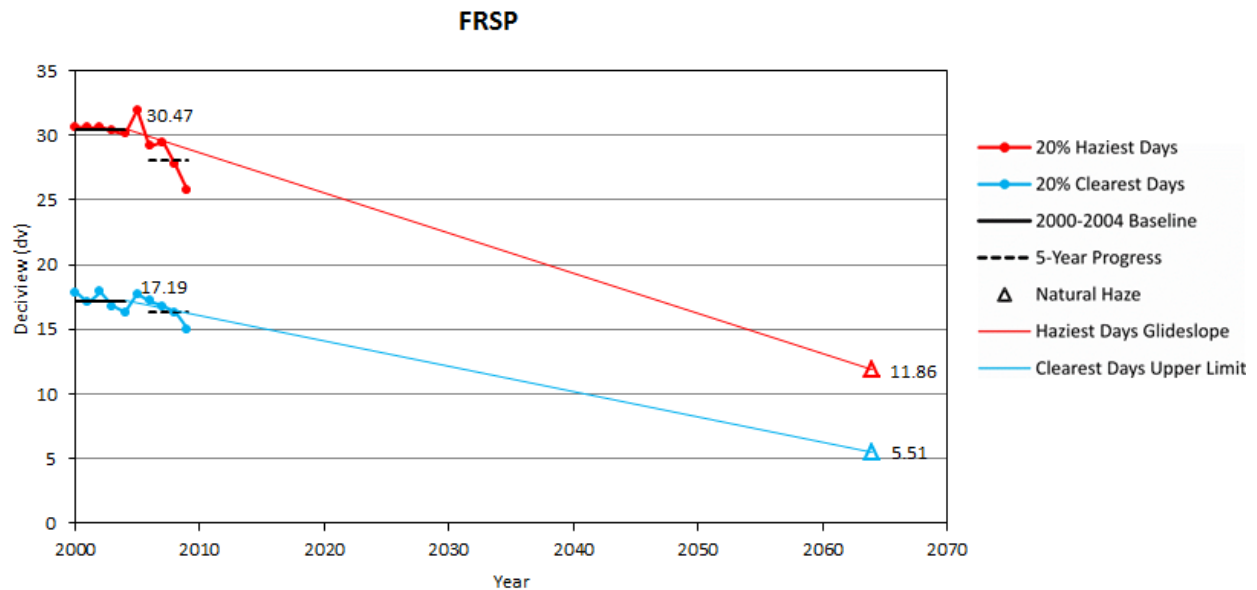


Figure 9c. Glideslopes to achieving natural visibility conditions in 2064 for the 20% hazeiest (red line) and the 20% clearest (blue line) days in FRSP. In the regional haze rule, the clearest days do not have a uniform rate of progress glideslope; the rule only requires that the clearest days do not get any worse than the baseline period. Also shown are measured values during the period 2000 to 2010. Data for APCO, EISE, FRSP, and GETT were taken from nearby sites (see Table 11). EISE and GETT have no data for the years 2000 and 2001; APCO has no data for the year 2000; and FRSP has no data for the year 2010. Data Source: http://vista.cira.colostate.edu/improve/Data/IMPROVE/summary_data.htm

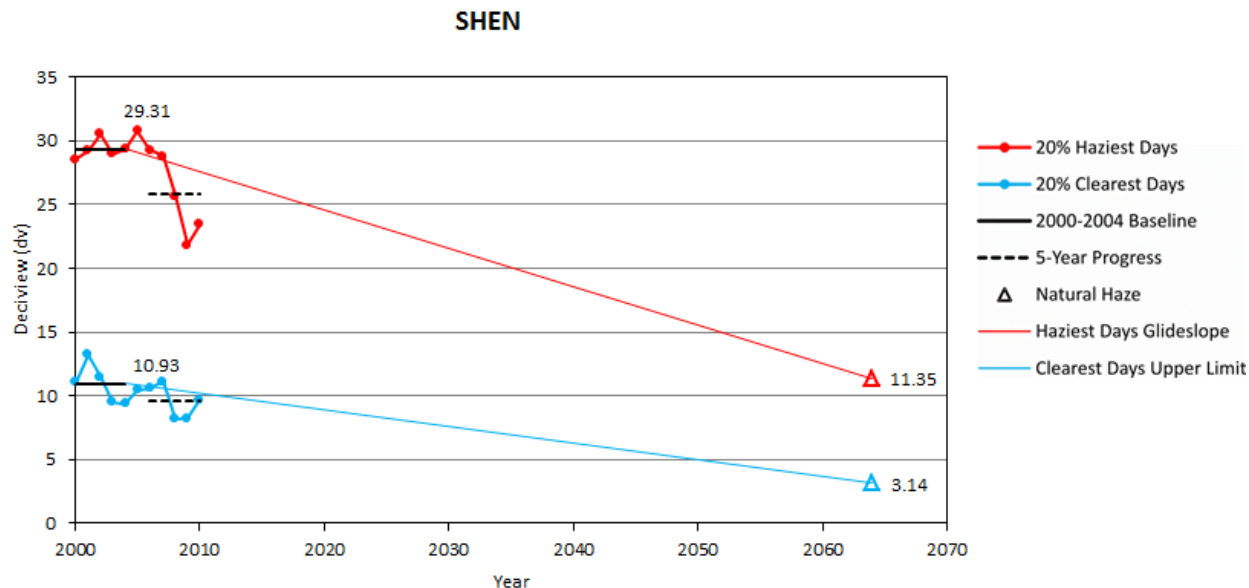


Figure 9d. Glideslopes to achieving natural visibility conditions in 2064 for the 20% hazeiest (red line) and the 20% clearest (blue line) days in SHEN. In the regional haze rule, the clearest days do not have a uniform rate of progress glideslope; the rule only requires that the clearest days do not get any worse than the baseline period. Also shown are measured values during the period 2000 to 2010. Data for APCO, EISE, FRSP, and GETT were taken from nearby sites (see Table 11). EISE and GETT have no data for the years 2000 and 2001; APCO has no data for the year 2000; and FRSP has no data for the year 2010. Data Source: http://vista.cira.colostate.edu/improve/Data/IMPROVE/summary_data.htm

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