



Air Quality Related Values (AQRVs) for Appalachian Highlands Network (APHN) Parks

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

Natural Resource Report NPS/APHN/NRR—2016/1152



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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Natural Resource Report NPS/APHN/NRR—2016/1152

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Summary

This report describes the Air Quality Related Values (AQRVs) of the Appalachian Highlands Network (APHN). AQRVs are those resources sensitive to air quality and include streams, lakes, soils, vegetation, fish and wildlife, and visibility. The APHN parks that are included in the NPS Inventory and Monitoring (I&M) Program, and discussed in this report, are Great Smoky Mountains National Park (GRSM), Big South Fork National River and Recreation Area (BISO), Blue Ridge Parkway (BLRI), and Obed Wild and Scenic River (OBRI). GRSM 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).

Sullivan et al. (2011a, 2011b) and Kohut (2007a) conducted risk assessments for acidification, eutrophication, and ozone (O_3) for all of the NCCN parks; their results are described in this report. This report also describes air pollutant emissions and air quality, and their effects on AQRVs. The primary pollutants likely to affect AQRVs include nitrogen (N) and sulfur (S) compounds (nitrate [NO_3^-], ammonium [NH_4^+], and sulfate [SO_4^{2-}]); ground-level O_3 ; 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 – Main Report” (Sullivan 2016).

Air pollution is an important concern in the APHN, and effects have been well-studied, especially within GRSM. Upwind emissions and deposition of both S and N are high in and around the APHN. In particular, S and N deposition are high at the upper elevations (especially above about 1,500 m) in GRSM, where cloud deposition contributes substantial amounts of S and N to acid-sensitive spruce-fir forests. Wet deposition of mercury (Hg) is also fairly high.

The most important air pollution concerns in the APHN include visibility, O_3 exposure, and acidification of soil and surface water. Pollution-caused haze levels are very high in GRSM. Ozone has harmed sensitive plant species. Many streams have acidified. There are known biological effects of acidification on acid-sensitive vegetation and aquatic biota in higher elevation, low-order stream watersheds. Although acidic deposition has declined substantially over the past two decades in this network, effects of S deposition may intensify in the future even under further reduced S loading. This is because soils in GRSM have adsorbed significant amounts of S over time, limiting acidification under relatively high levels of S deposition. As this adsorption capacity is exhausted, however, continued S input, albeit at lower levels, will trigger delayed acidification responses in soils and drainage waters.

Ozone exposures and risk to sensitive vegetation reported by Kohut (2007a) were moderate to high within the APHN, depending on the park unit and choice of exposure index on which to base the assessment. Based on both O_3 cumulative exposure and Kohut's (2007a) risk ranking index, concern for O_3 effects on vegetation is high in all of the I&M parks that occur in the APHN, except BLRI.

GRSM contains some of the largest tracts of old-growth forest in the eastern United States. Old-growth spruce-fir forests predominate at elevations above 1,500 m in the park. Mixed hardwood

forests cover the lower slopes. Although atmospheric deposition of both S and N has been high in the park, deposited N has the largest influence on stream chemistry because watershed retention of atmospherically deposited S has been high (Flum and Nodvin 1995). Streams in GRSM draining old-growth coniferous forests commonly have had NO_3^- concentrations above 50 $\mu\text{eq/L}$, which has been higher than at most lower elevation sites.

Background

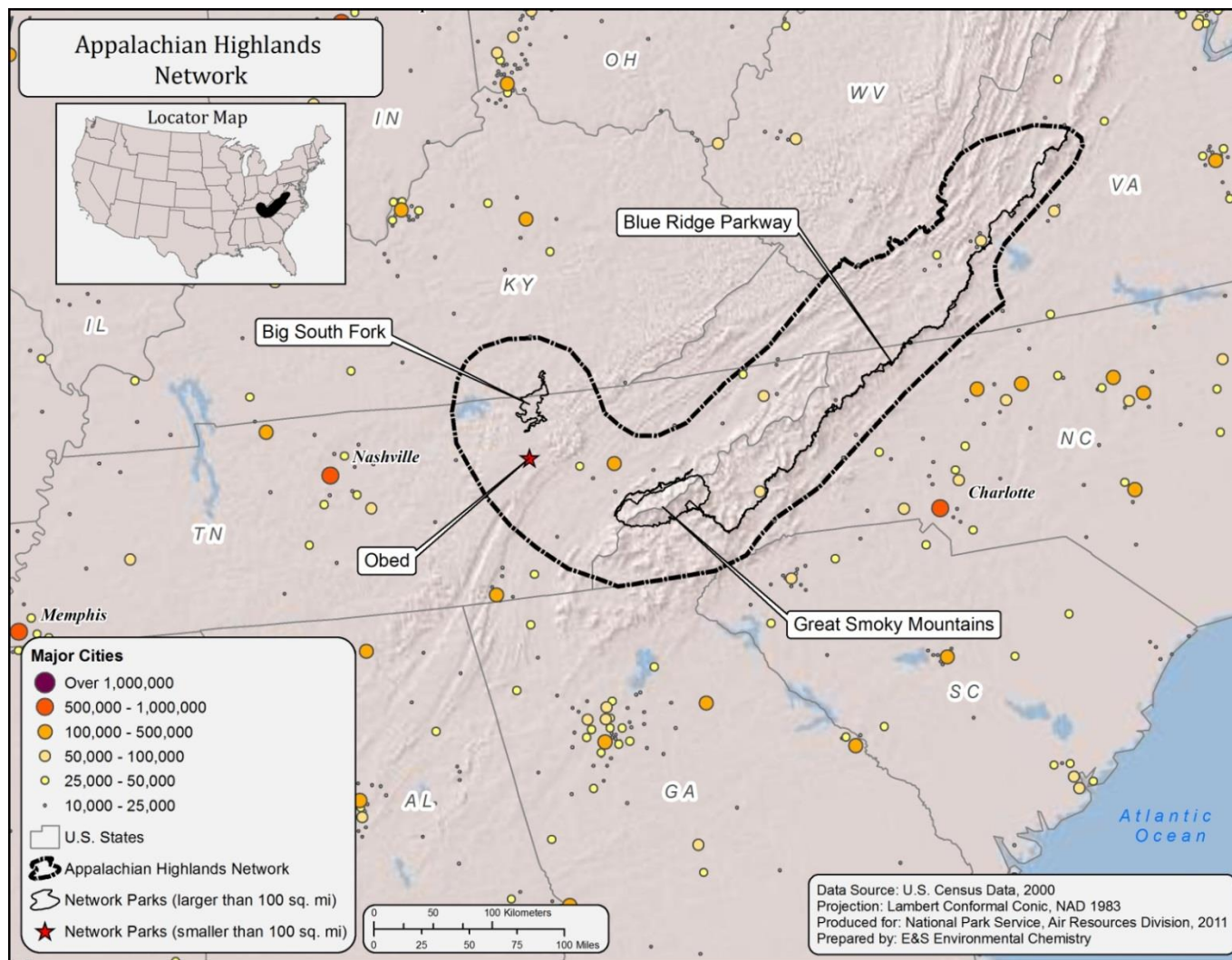
The Appalachian Highlands Network (APHN) contains three parks that are larger than 100 square miles: Great Smoky Mountains National Park (GRSM), Big South Fork National River and Recreation Area (BISO), and Blue Ridge Parkway (BLRI). It also contains one smaller park: Obed Wild and Scenic River (OBRI). 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. Within the APHN, effects of air pollutants on air quality related values (AQRVs) have only been well-studied in GRSM. Map 1 shows the network boundary, the location of each park, and population centers having more than 10,000 people.

The only Class I park in the Network, GRSM, is an international biosphere reserve and is the most heavily visited national park in the United States. The park contains the largest remaining area of old-growth spruce-fir forest in the United States (Shaver et al. 1994). Air pollution constitutes a major threat to the health of natural resources in this park, and elsewhere in the APHN. As a consequence, air pollution effects research in GRSM has been substantial. Shaver et al. (1994) reported a case study that described how the National Park Service (NPS) uses scientific data in regulatory arenas to address air pollution problems in GRSM (and other Class I areas).

Atmospheric Emissions and Deposition

Sulfur dioxide (SO_2) emissions in and surrounding the APHN, and S deposition within the network, have both been high. Malm et al. (2002) analyzed spatial patterns in atmospheric sulfate (SO_4^{2-}) concentrations throughout the United States from 1988 to 1999 and also atmospheric SO_2 emissions from 1990 to 1999. The 90th percentile summer atmospheric SO_4^{2-} concentrations throughout the United States were highest in the Ohio River Valley and in central Tennessee, where emissions of SO_2 have been especially high (Malm et al. 2002). Although S emissions have been substantially reduced by requirements of the Acid Rain Program, this region still has the highest emissions levels in the country (Burns et al. 2011). These emissions have the potential to impact sensitive resources in the APHN. The network is also surrounded by many large urban areas and point sources of both S and N emissions.

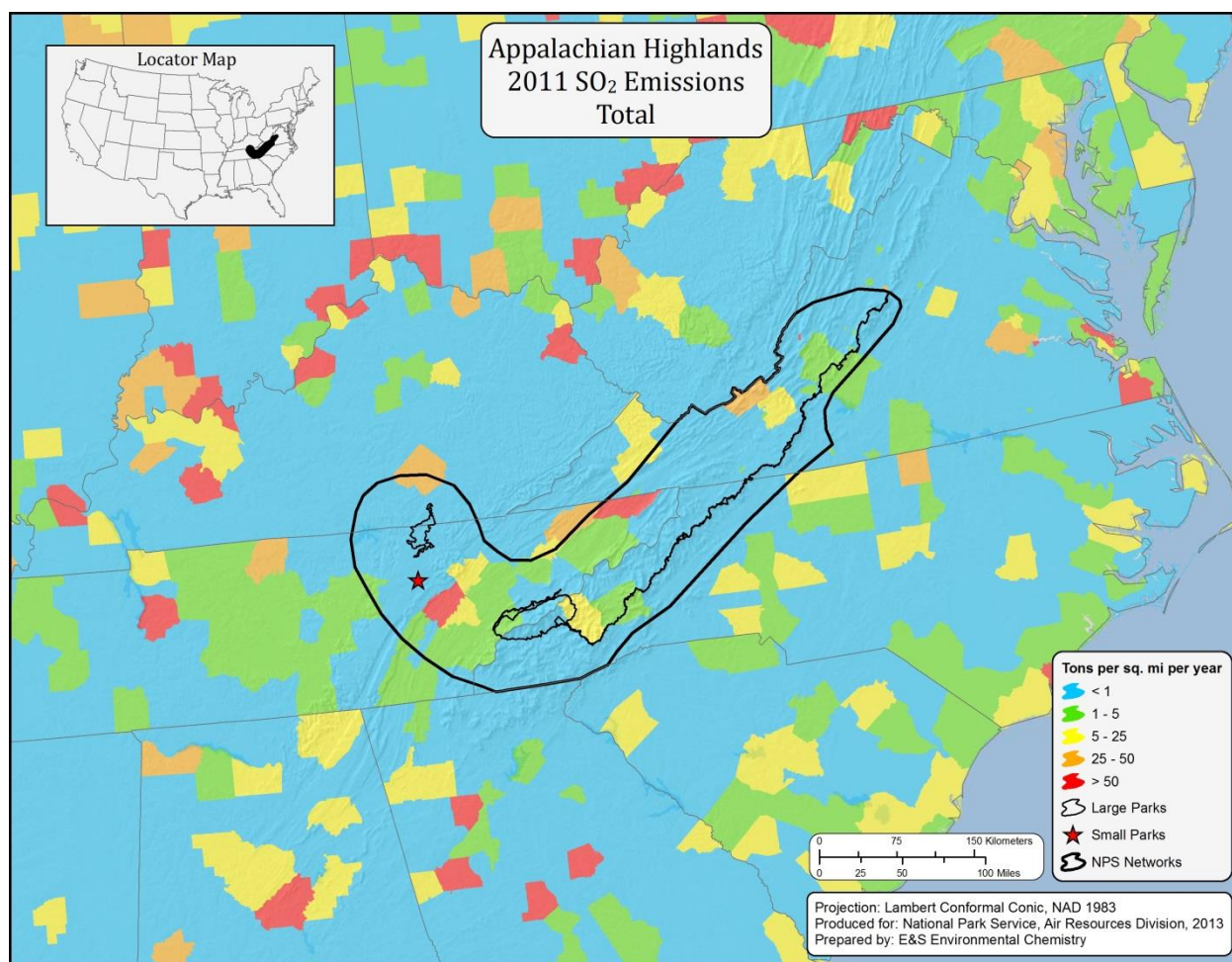
The atmospheric concentrations of SO_4^{2-} in this region during the 1990s were twice as high as concentrations in the northeastern and coastal southeastern United States. However, during the 1990s, SO_2 emissions in Ohio and Indiana, upwind of the APHN, decreased by 35% and 44%, respectively (Malm et al. 2002). Additional emissions reductions have been enacted in more recent



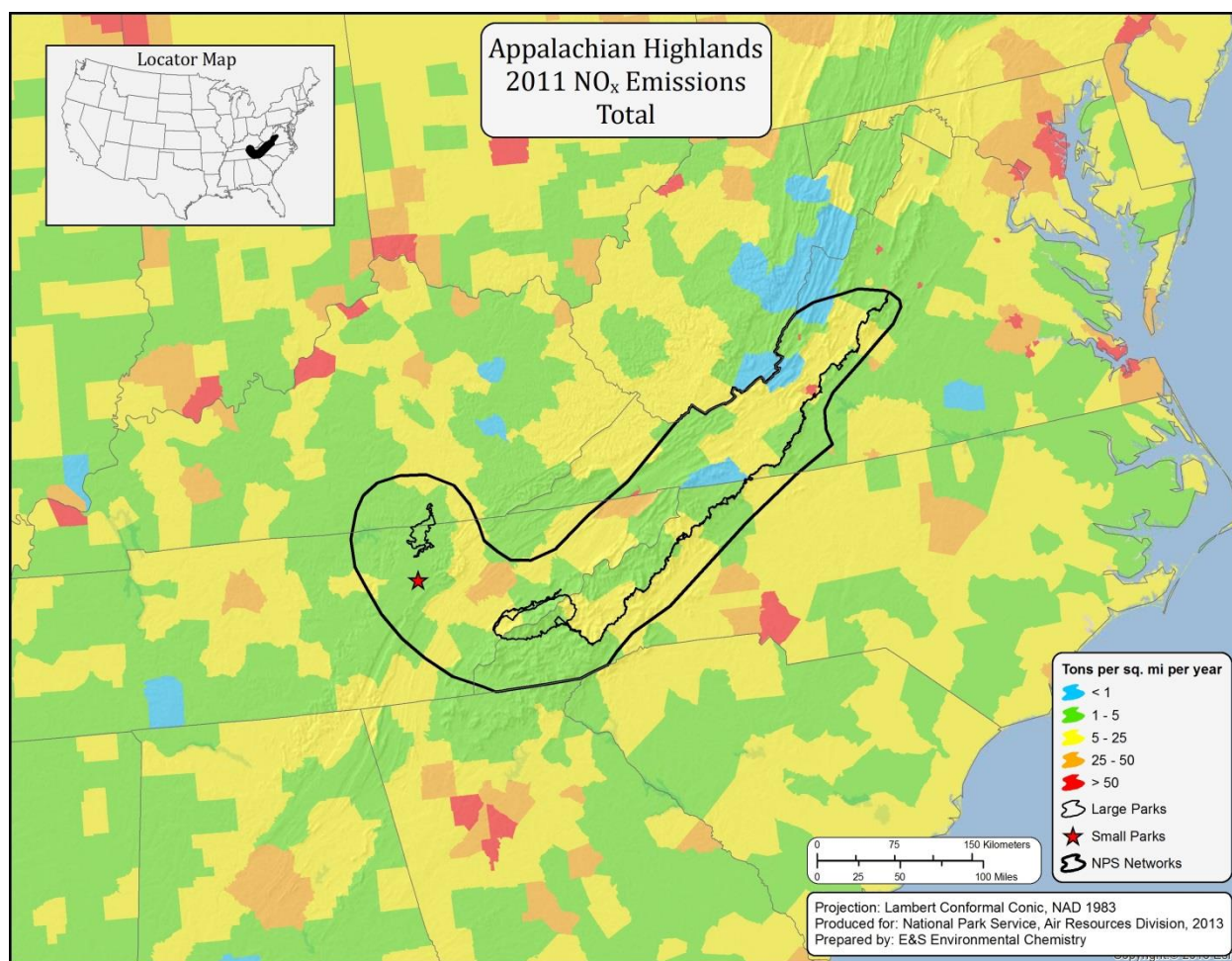
Map 1. Network boundary and locations of parks and population centers greater than 10,000 people.

years in conjunction with the North Carolina Clean Smoke Stacks Act and a legal settlement between North Carolina and the Tennessee Valley Authority. As a result, ambient SO₂ concentrations in the Southeast decreased by more than 50% between the periods 1989-1991 and 2007-2009 (Burns et al. 2011).

County-level emissions near the APHN, 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, oxidized nitrogen (NO_x), and reduced N (NH₃), respectively. Several counties to the north and west of APHN parks had relatively high SO₂ emissions (> 50 tons per square mile per year [tons/mi²/yr]; Map 2). Spatial patterns in NO_x emissions were generally similar, with highest values to the northwest of APHN parks (Map 3). Emissions of NH₃ near APHN parks were somewhat lower, with most counties showing emissions levels below 8 tons/mi²/yr (Map 4).



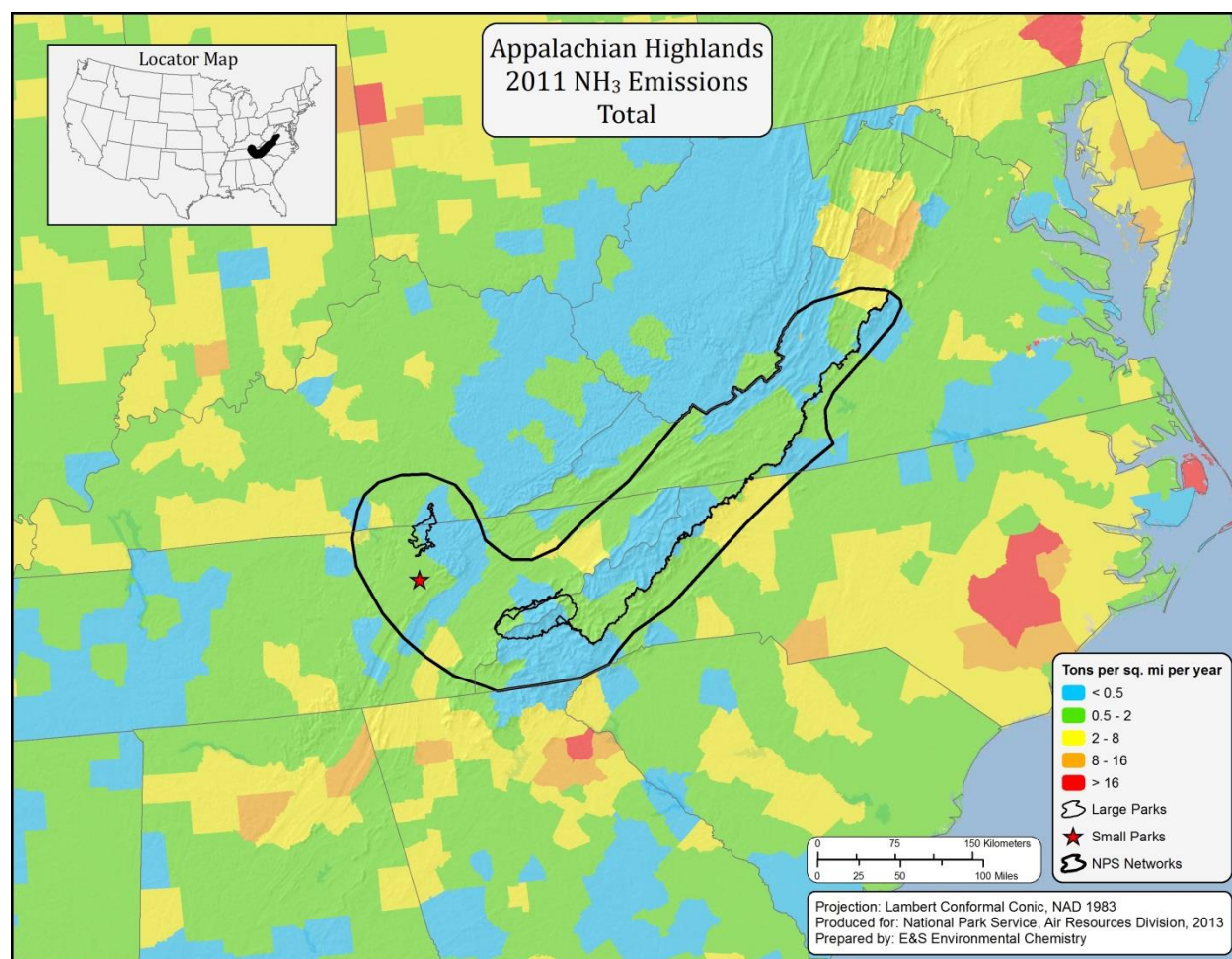
Map 2. Total SO₂ emissions, by county, near the APHN for the year 2011. Data from EPA's National Emissions Inventory.



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

Total wet plus dry S deposition throughout much of the APHN ranged from about 10 to 15 kg/ha/yr in 2002 (Sullivan et al. 2011b). Some locations within the network had estimated wet plus dry S deposition higher than that. Total wet plus dry N deposition within the network ranged from as low as 2 to 5 kg N/ha/yr per year to as high as 10 to 15 kg N/ha/yr (Sullivan et al. 2011b). In addition, it is known that cloud deposition, which is not represented in the total deposition values depicted on the maps of Sullivan et al. (2011b), can be quite high at high-elevation sites (especially those higher than 1,500 m) that occur in and around GRSM. At the highest elevation locations, the total S and N deposition, including cloud inputs, might each be as much as double the wet plus dry deposition values that were mapped by Sullivan et al. (2011a, 2011b) from National Atmospheric Deposition Program (NADP) interpolations of wet and Community Multiscale Air Quality (CMAQ) simulations of dry deposition. However, because of large more recent emissions reductions achieved by the Acid Rain Program and other air quality improvement programs, total S deposition decreased about 40% in the Southeast between the periods 1989-1991 and 2007-2009 (Burns et al. 2011). Total N deposition decreased about 19%. This more modest decrease in N deposition reflects the fact that air quality management programs for N focused only on NO_x sources (vehicles, power plants, industry);

ammonia sources (agriculture, feedlots), which also contribute to total N deposition, are unregulated. Current estimates, however, for both S and N deposition clearly show significant decreases from past levels.



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

Recently, Schwede and Lear (2014) documented a hybrid approach developed by the 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 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.

Atmospheric S, and to a lesser extent N, deposition levels have declined at APHN 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 -4.24 kg S/ha/yr (-35.6%) at BLRI to -8.21 kg S/ha/yr (-53.8%) at OBRI. Estimated total N deposition decreased over that same time period by -0.79 kg N/ha/yr (-7.4%) at GRSM to -2.16 kg N/ha/yr (-18.9%) at OBRI. Oxidized and reduced N showed opposite patterns, with oxidized N decreasing and reduced N increasing at all of the parks in the network since the monitoring period 2000-2002.

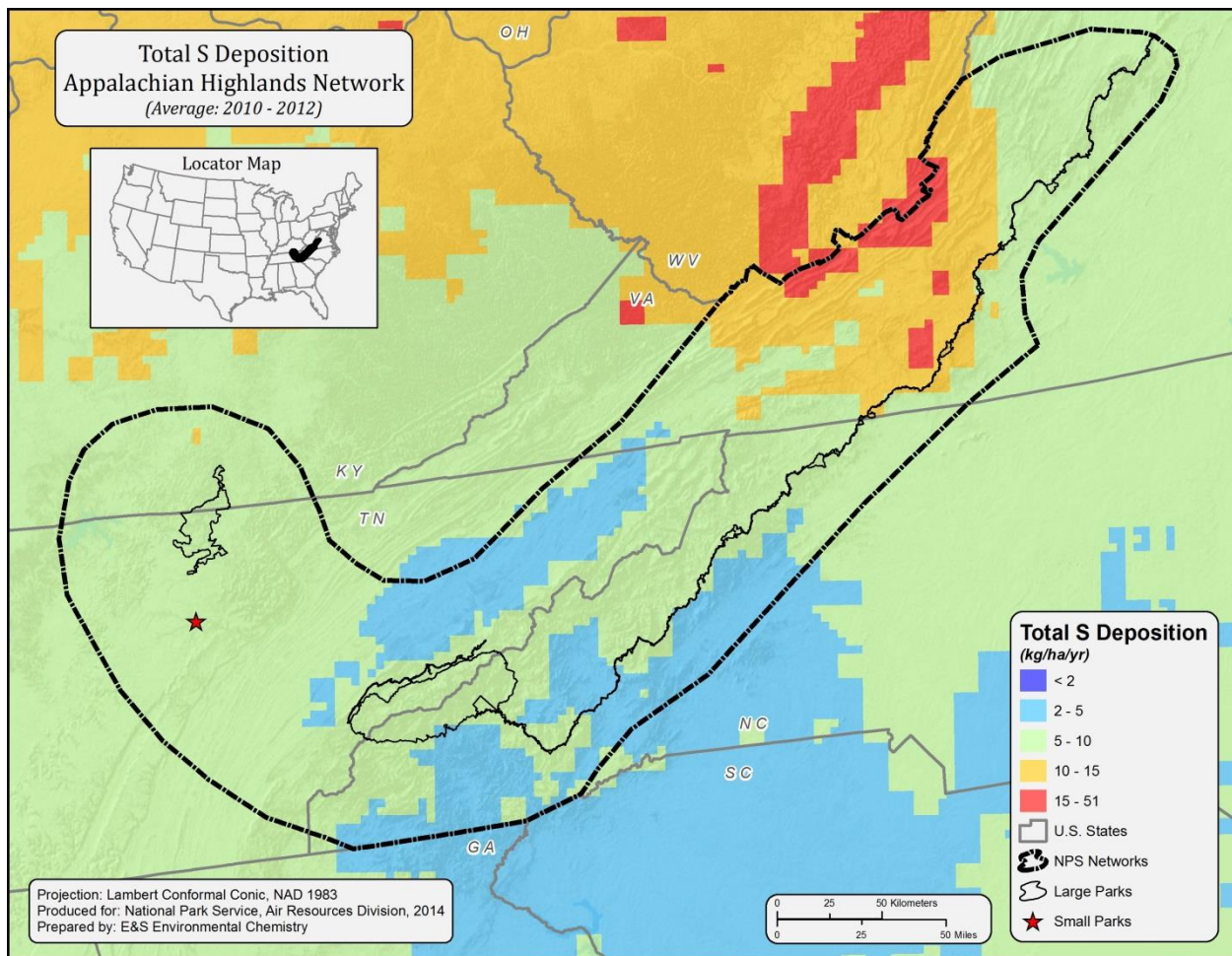
Total S deposition in and around the APHN for the period 2010-2012 was generally highest (> 10 kg S/ha/yr) to the northwest and lowest (< 5 kg S/ha/yr) to the southeast of the network area (Map 5). Total S deposition during that time period varied substantially in BLRI.

Oxidized inorganic N deposition for the period 2010-2012 was in the range of 5 to 10 kg N/ha/yr throughout much of the park land within the APHN (Map 6). Most areas received about 2 to 5 kg N/ha/yr of reduced inorganic N from atmospheric deposition during this same period (Map 7); total N deposition was in the range of 10 to 15 kg N/ha/yr at some park locations (Map 8). Other areas received 5 to 10 kg N/ha/yr of total N deposition.

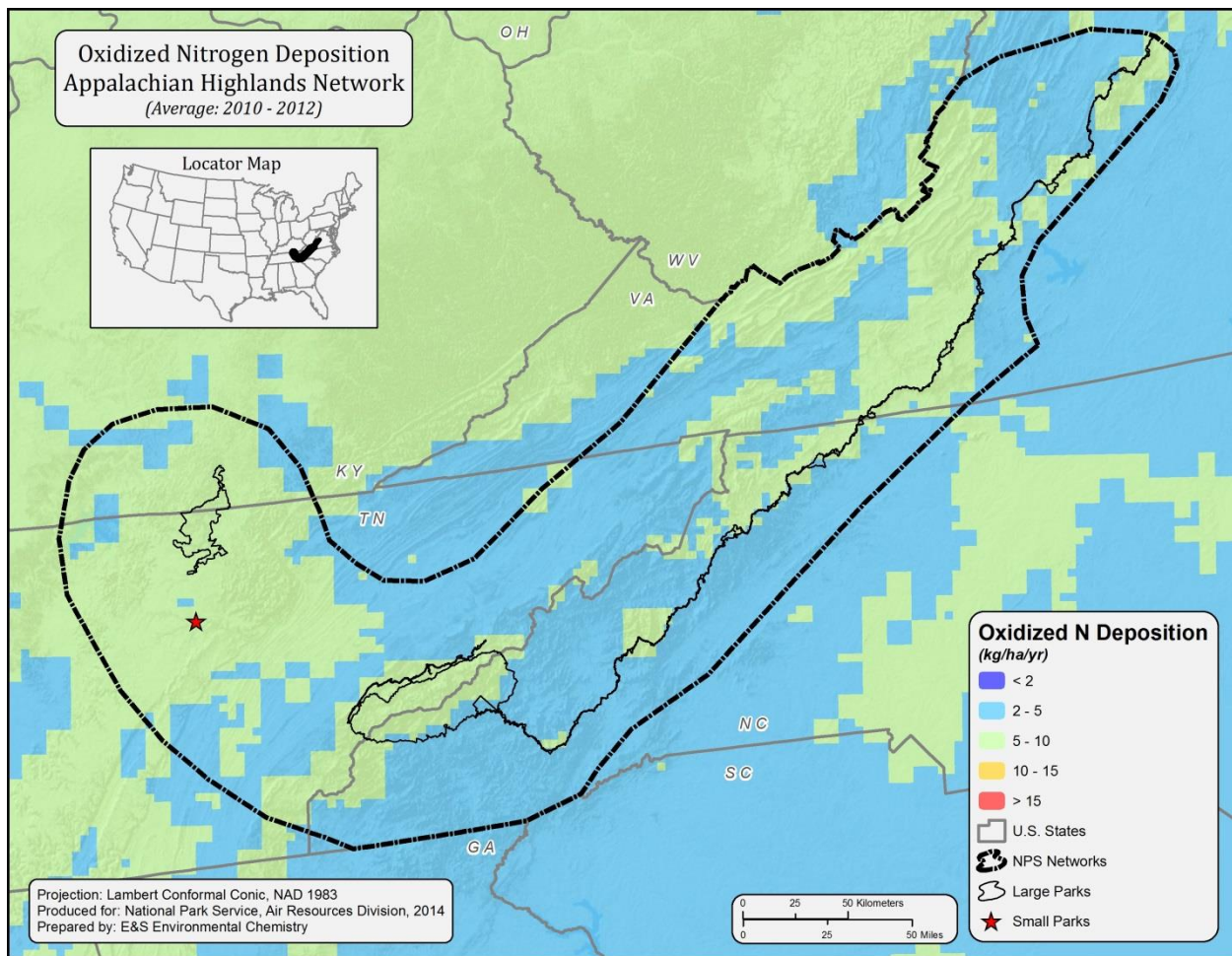
Weathers et al. (2006) developed an empirical modeling approach, based on 300-400 throughfall measurements, to estimate total (wet, dry, cloud) deposition of S and N to complex terrain of GRSM. Throughfall deposition measurements taken during summer, combined with landscape variables such as elevation, forest type, and slope, explained about 40% of the variation in total deposition estimates. Model estimates were scaled to measured wet and estimated dry deposition values from NADP and Clean Air Status and Trends Network (CASTNET) monitoring sites, respectively. Resulting maps showed substantial spatial variability, ranging up to 31 kg N/ha/yr and 42 kg S/ha/yr across the landscapes of this park (Map 9). Thus, atmospheric loadings of both S and N at high elevation locations in GRSM have been among the highest of any wildland area in the United States. Much of this deposition has been from dry and cloud deposition processes, which are particularly efficient modes of deposition in spruce-fir forests along the ridge tops. Because of recent emissions reductions, these modeled deposition estimates do not reflect current conditions, but are important in assessing the long-term effects of acid deposition in the region.

Table 1. Average changes in S and N deposition between 2001 and 2011 across park grid cells at APHN 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.

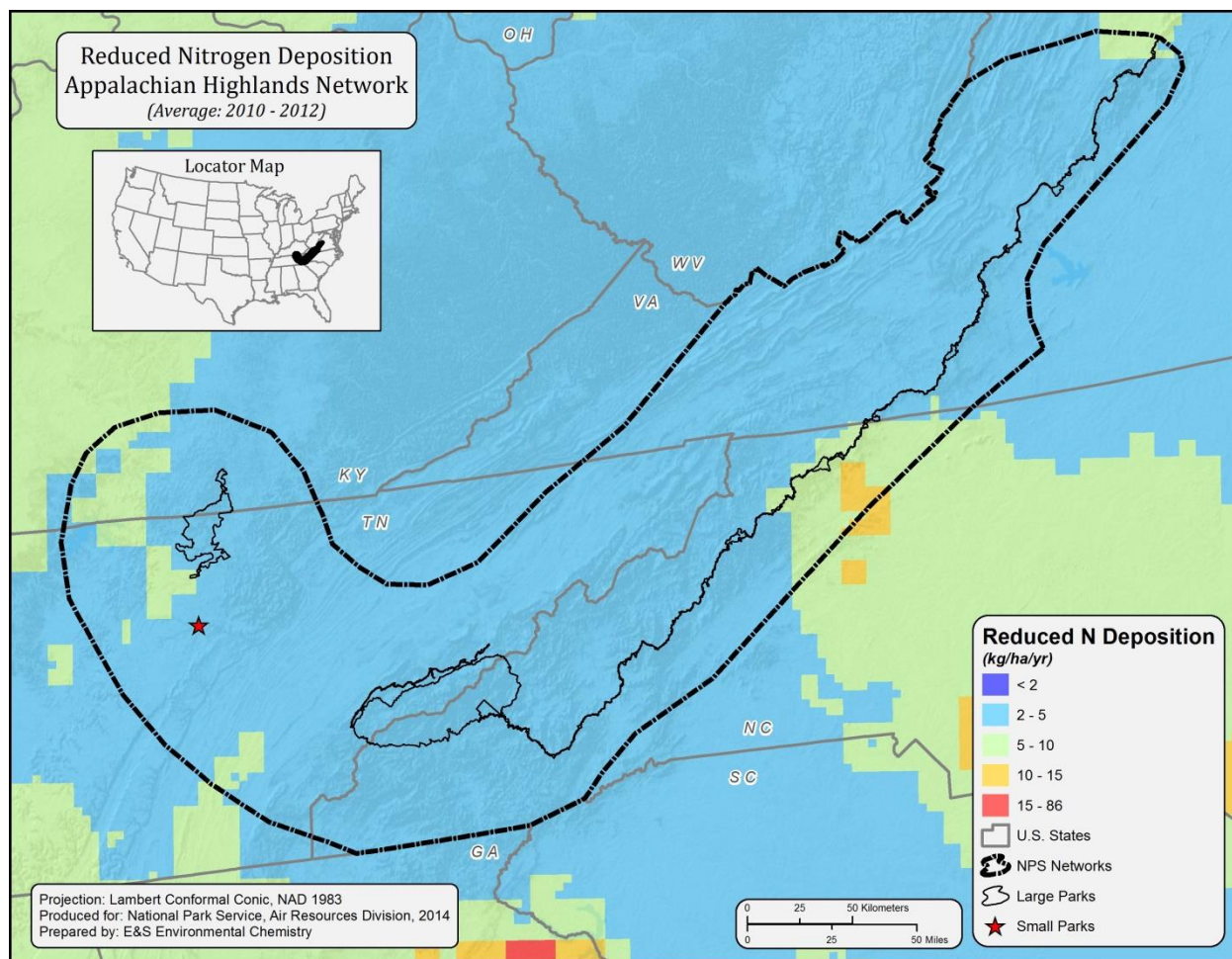
Park Code	Park Name	Parameter	2001 Average (kg/ha/yr)	2011 Average (kg/ha/yr)	Absolute Change (kg/ha/yr)	Percent Change	2011 Minimum (kg/ha/yr)	2011 Maximum (kg/ha/yr)	2011 Range (kg/ha/yr)
BISO	Big South Fork	Total S	15.62	7.80	-7.82	-50.1%	7.17	8.56	1.39
		Total N	11.58	9.66	-1.92	-16.6%	8.98	10.84	1.85
		Oxidized N	8.34	5.53	-2.81	-33.7%	5.21	5.99	0.78
		Reduced N	3.24	4.13	0.89	27.7%	3.74	5.31	1.58
BLRI	Blue Ridge	Total S	12.31	8.06	-4.24	-35.6%	4.09	14.66	10.57
		Total N	10.97	9.26	-1.71	-15.8%	6.38	12.73	6.35
		Oxidized N	7.61	5.15	-2.46	-32.2%	3.76	6.73	2.96
		Reduced N	3.36	4.11	0.74	21.2%	2.42	7.82	5.40
GRSM	Great Smoky Mountains	Total S	12.92	7.39	-5.52	-42.8%	4.02	9.19	5.17
		Total N	10.69	9.89	-0.79	-7.4%	6.31	11.68	5.37
		Oxidized N	7.64	5.89	-1.75	-22.9%	3.62	6.89	3.27
		Reduced N	3.04	4.00	0.96	32.1%	2.68	4.85	2.17
OBRI	Obed	Total S	15.25	7.04	-8.21	-53.8%	6.89	7.63	0.74
		Total N	11.42	9.26	-2.16	-18.9%	8.95	10.33	1.38
		Oxidized N	8.39	5.22	-3.16	-37.7%	5.06	5.59	0.53
		Reduced N	3.04	4.03	1.00	32.9%	3.79	4.74	0.95



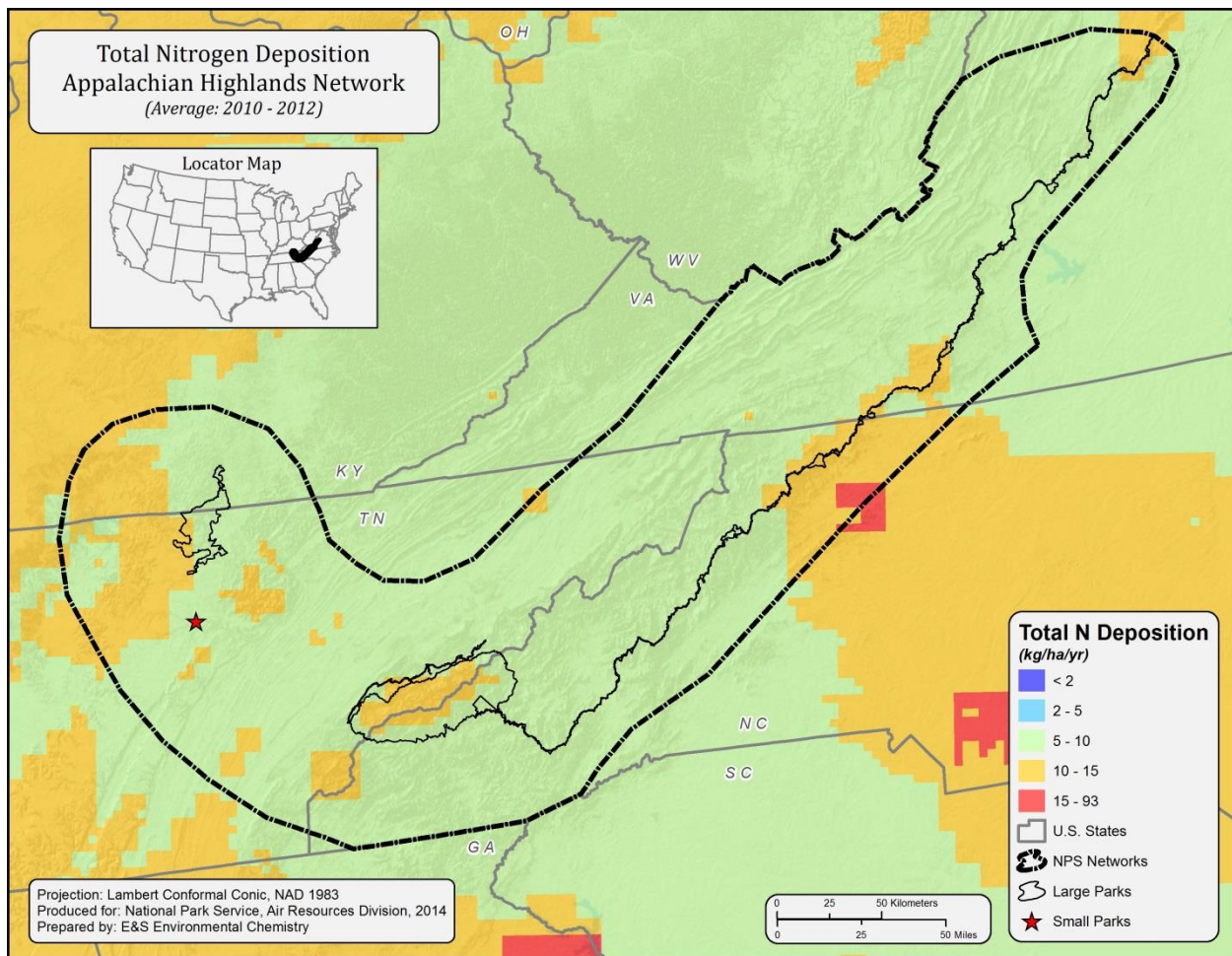
Map 5. Total S deposition for the three-year period centered on 2011 in and around the APHN. (Source: Schwede and Lear 2014)



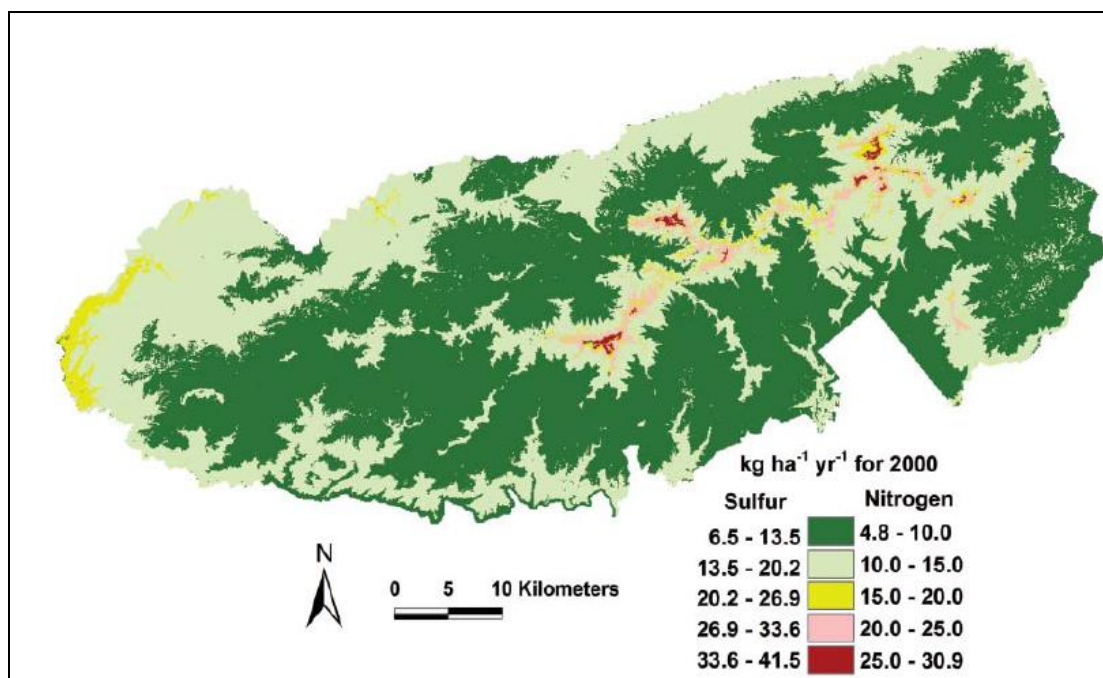
Map 6. Total oxidized inorganic N deposition for the three-year period centered on 2011 in and around the APHN. (Source: Schwede and Lear 2014)



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



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



Map 9. Total (wet, dry, and cloud) inorganic N (and S) deposition estimated for Great Smoky Mountains National Park for the year 2000 (Source: Weathers et al. 2006, Weathers and Lynch 2011). Although N and S deposition have decreased substantially since 2000, the map shows the large variability in deposition levels throughout the park, with higher elevation ridgetop areas receiving higher inputs of N and S.

Cloud water deposition was measured at three high elevation sites in the Appalachian Mountains in the Mountain Acid Deposition Program (MADPro). One of those sites was at Clingmans Dome in GRSM. Seasonal cloud water deposition at that site was very high for both SO_4^{2-} ($> 50 \text{ kg/ha}$) and nitrogen oxides (NO_x ; $> 25 \text{ kg/ha}$). Baumgardner et al. (2003) concluded that total deposition of acidic anions at high elevation ($> 1500 \text{ m}$) in GRSM may be 6 to 20 times greater than the deposition at low elevation, with this difference mainly attributed to cloud deposition at the high elevations.

Atmospheric deposition of mercury (Hg) is also important for resource protection in the APHN. NPS (2010) reported long-term trends in concentrations of Hg in wet deposition during the periods beginning in 1996 to 2003, and running through 2008, for nine national parks. 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. Highest Hg concentration in precipitation was reported for Everglades National Park (in the South Florida and Caribbean Network), followed by GRSM.

Acidification

Based on a coarse screening assessment by Sullivan et al. (2011b), the Ecosystem Sensitivity ranking of the APHN was Very High for acidification risk, the highest among all networks. This is because vegetation includes forest expected to contain sugar maple (*Acer saccharum*), one of the tree species thought to be especially sensitive to acidification effects from S and N deposition. In addition, there are high-elevation areas containing sensitive red spruce (*Picea rubens*) and many high-elevation and low-order acid-sensitive streams on relatively steep terrain.

The overall park Summary Risk ranking for the parks in this network was Very High for BLRI and GRSM and High for the other two parks. Based on the Pollutant Exposure and Ecosystem Sensitivity rankings, potential acidification from acidic deposition is an important concern for the parks in this network. In most regions of the United States that have experienced acidification effects from air pollution, those effects have mainly been due to S deposition. There are also, however, some regions, especially at high elevation in GRSM, where both atmospheric S and N have contributed substantially to the observed acidification. While rankings are an indication of risk, park-specific data, particularly data on ecosystem sensitivity, are needed to fully evaluate risk from acidification.

All four I&M parks in this network (BLRI, GRSM, BISO, and OBRI) were ranked High in park-specific acid Pollutant Exposure (Table 2; Sullivan et al. 2011b), indicating high levels of atmospheric S and N deposition. However, the failure to include cloud deposition at very high-elevation locations in GRSM likely biased the acid Pollutant Exposure ranking low for that park. Thus, the true acid Pollutant Exposure ranking for parts of GRSM is more likely Very High.

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
<i>Big South Fork</i>	BISO	High	Very High
<i>Blue Ridge Parkway</i>	BLRI	High	Very High
<i>Great Smoky Mountains</i>	GRSM	High ³	Very High
Obed	OBRI	High	Very 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 m².

³ The acid Pollutant Exposure of portions of GRSM located at high elevation are likely higher than was suggested by Sullivan et al. (2011b) because of substantial cloud deposition of S and N.

Acidification of Terrestrial Ecosystems

Some research has been conducted within the APHN on the effects of S and N on lichens. McCune et al. (1997) found air pollution-tolerant epiphytic lichen species to be present, along with relatively low epiphytic lichen species richness, in urban and industrial areas within Georgia, North Carolina, South Carolina, Tennessee, and Virginia. In contrast, air pollution-sensitive species were more

common, and richness was higher, in rural areas. These effects on lichens may be due to both acidification and nutrient enrichment impacts of enhanced S and N input.

Land cover within the parks that occur in the APHN is primarily forested. These forests contain vegetation types that include red spruce and sugar maple, two tree species thought to be especially sensitive to acidification and accompanying soil base cation depletion. Much of GRSM, in particular, is covered by vegetation types likely to contain either red spruce or sugar maple, with the exception of lands around parts of the park boundary. Red spruce is confined to the higher elevations, generally higher than about 1,300 m. Much of this higher elevation land is distributed along the Appalachian Mountain ridgeline.

The major effects of acidic deposition on vegetation are mediated through the soil (National Science and Technology Council 1998) and are considered to be indirect effects. High elevation soils in GRSM are mainly shallow and highly weathered, with substantial S adsorption capacity and limited base cation supply (Elwood 1991). Acidic deposition has contributed to a decline in the availability of calcium (Ca^{2+}) and other base cations in the soils of acid-sensitive forest ecosystems due to leaching of base cations from foliage and from the primary rooting zone, and by the mobilization of Al from soils to soil solution and drainage water (Eagar and Adams 1992, National Acid Precipitation Assessment Program [NAPAP] 1998). Aluminum mobilization from acid soils can impede Ca^{2+} and magnesium (Mg^{2+}) uptake by plant roots and potentially induce deficiencies in these nutrients. Both N and S deposition have contributed to these effects in the APHN. As a consequence, foliar Ca^{2+} levels and soil and root Ca:Al ratios are considered low to deficient over large portions of the spruce-fir region in the eastern United States, including within the APHN (Cronan and Grigal 1995, Joslin et al. 1992, NAPAP, 1998).

Researchers have concluded that the spruce-fir forests in GRSM have been affected by atmospheric S and N deposition in at least two important ways (Eagar and Adams 1992, Shaver et al. 1994):

1. inputs of N and other nutrients exceed normal litterfall inputs, thereby altering nutrient cycling, and
2. pulses of high NO_3^- and SO_4^{2-} concentrations in soil water have caused periodic increases in aluminum (Al) concentration in soil water which could inhibit root growth and plant nutrient base cation uptake.

Calcium must be dissolved in soil water in order to be taken up by roots. Aluminum in soil solution reduces Ca^{2+} uptake by competing for binding sites in the cortex of fine roots. Tree species may be adversely affected if high Al-to-nutrient ratios limit the uptake of Ca^{2+} and Mg^{2+} (Garner 1994, Shortle and Smith 1988). A reduction in Ca^{2+} uptake suppresses cambial growth, reduces the rate of wood formation, decreases the amount of functional sapwood and live crown, and predisposes trees to disease and injury, especially when the functional sapwood becomes less than 25% of the cross-sectional stem area (Smith 1990).

A variety of factors are known to predispose soils of high-elevation spruce-fir forests in GRSM to potential Al toxicity and Al-induced inhibition of cation uptake. These factors include features of the

climate (high precipitation, low temperature), vegetation (coniferous litter), bedrock (low base cation production), and soil forming processes such as podzolization (Eagar et al. 1996). Dissolved Al concentrations measured in soil solution at spruce-fir study sites in GRSM frequently exceeded 50 μM and sometimes exceeded 100 μM (Johnson et al. 1991a, Joslin and Wolfe 1992). All studies reviewed by Eagar et al. (1996) showed a strong correlation between Al concentrations and NO_3^- concentrations in soil solution. They speculated that the occurrence of periodic large pulses of NO_3^- in solution were important in determining soil Al chemistry in this region.

Dendro-chronological analyses of tree cores collected from permanent plots in GRSM (37 trees cores from moderate elevation [~ 1500 m]; 35 tree cores from high-elevation sites [~ 2000 m]), demonstrated a positive correlation between temporal and spatial trends in red spruce growth and acidic deposition, with a greater response in trees on ridges as compared with trees in draws (Eagar et al. 1996, Webster et al. 2004). In general, ridges are naturally more acidified, receive higher levels of acidic deposition, and have shallower soils with lower base saturation (BS; Webster et al. 2004).

From the 1940s to 1970s, red spruce growth declined in the southern Appalachian Mountains, as upwind emissions of both NO_x and SO_2 increased. The growth decline started earlier at higher elevations (around 1940s and 1950s) and was steeper, while the growth decline developed about 20 years later at lower elevation sites. After the 1980s, growth increased substantially at both the higher and lower elevations sites, corresponding to a decrease in SO_2 emissions throughout the eastern United States, while NO_x emissions held fairly steady. Annual emissions of sulfur oxides (SO_x) + NO_x explained about 43% of the variability in tree ring growth at high elevation between 1940 and 1998, while climatic variability accounted for about 8% of the growth variation for that period. At low elevation, changes in radial growth could be explained by climatic variables only, and there was no correlation with national SO_x and NO_x emissions trends (Eagar et al. 1996, Webster et al. 2004).

Results of modeling by Sullivan et al. (2002b), using the Nutrient Cycle Model (NuCM; Johnson et al. 1993b, Liu et al. 1991), together with the results of NuCM simulations published for other watersheds in the southern Appalachian Mountain region, suggested that spruce-fir forests in the region are likely to experience decreased Ca:Al ratios in soil solution under virtually all strategies of reduced future acidic deposition considered in the modeling effort. This was partly because S adsorption on soils is likely to decline, even with dramatically reduced S deposition, allowing increased SO_4^{2-} leaching. In addition, many spruce-fir forests in the region are at least partially N-saturated, and continued N deposition at moderate or high levels would be expected to contribute to elevated NO_3^- concentrations in soil water, which could further enhance base cation leaching and mobilization of Al from soils to soil solution (Sullivan et al. 2002b). These processes will be exacerbated by the already low values of BS in the soils of many of these forests. Thus, results of these modeling efforts suggest that changes to forest soils and soil solution will likely continue to occur. It is not clear, however, to what extent these changes in the chemistry of soils and soil solutions might actually impact forest growth and health. The state of scientific understanding on this topic suggests that such chemical changes would increase the likelihood that the growth and/or health of spruce-fir forests would be adversely impacted, perhaps making them more susceptible to other stressors associated with such factors as insect pests, pathogens, or extreme climatic conditions.

However, the occurrence of low BS and low Ca:Al ratio in soil solution will not necessarily be sufficient to cause widespread impacts. Many factors in addition to soil and soil solution acid-base chemistry are important in this regard. Fraser fir (*Abies fraseri*) stands killed by the balsam woolly adelgid (*Adelges piceae*) are largely being replaced by vigorous re-growth of young stands of that species (Van Miegroet et al. 2007). To what extent spruce or fir mortality in the southern Appalachian Mountains will result in a species mix similar to what existed prior to the mortality remains to be seen.

The limited available empirical data suggest that the kinds of changes in soil solution chemistry projected by the NuCM model for spruce-fir stands in the APHN region are consistent with the kinds of changes that have been associated in the past with reductions in forest growth. The weight of evidence for spruce-fir forests suggests that continued adverse impacts on soil solution chemistry are likely, and adverse impacts on forest growth and health are possible (Sullivan et al. 2002b).

Scientists are concerned about the potential effects of soil acidification on forest health in the APHN. However, forest health is a complicated concept. It can be reflected in a variety of physiological indicators, including, for example, changes in the growth rate of trees, foliar damage, branch dieback, susceptibility to insects or disease, or tree mortality. Similarly, forest health can be affected by a host of potential stressors, of which air pollution is only one possibility. Climatic conditions, stand competition, outbreak of non-native pathogens, and forest management (alone or in combination) often contribute greatly to observed forest health problems. Attempts to document, and in particular to quantify, the effects of air pollution on forest health have encountered considerable complexity and uncertainty. Nevertheless, such efforts have produced evidence that suggests that red spruce, and also sugar maple, in some areas in the eastern United States have experienced declining health as a consequence of acidic deposition (Eagar et al. 1996, Sullivan et al. 2002b).

Base saturation values less than 10% predominate in the B horizon in areas where soil and surface water acidification from acidic deposition have been most pronounced, including red spruce forests in the southern Appalachian Mountains (Sullivan et al. 2003). Decreases in concentrations of exchangeable base cations in the Oa and B soil horizons over the past several decades have been common and widespread in the eastern United States. Acidic deposition has been shown to be an important factor causing the observed decreases in concentrations of exchangeable base cations on soils. 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 resupply by weathering, which is a slow process.

The natural downward movement and deposition of Al within the soil profile has been altered by acidic deposition, resulting in greater availability of inorganic Al within soil and transport of this form of Al from the soil to surface waters. Atmospheric deposition of N has also decreased C:N ratios in soils, and contributed to an increase in net nitrification and associated production of acidity in soils. Nitrogen availability in excess of ecological demand (N saturation) has become common and widespread, as evidenced by elevated NO_3^- concentrations in surface waters during the growing season in many areas, including within the APHN.

Johnson et al. (1999) explored, through simulation modeling, potential effects of changes in S, N, and base cation deposition on two contrasting forest ecosystems: a highly acidic red spruce site (1740 m elevation) at Noland Divide in GRSM and a moderately acidic mixed hardwood site at the Coweeta hydrological research station (720 m elevation) in North Carolina. The simulations were performed using the NuCM model. Results for the highly acidic Noland Divide site suggested that S and N deposition are the major drivers of soil solution concentrations of Al at this site, and that atmospheric base cation deposition is the major driver of soil solution concentrations of base cations. Results differed at the less acidic Coweeta site, where Al was unimportant, and S and N deposition had a much larger impact than base cation deposition on simulated soil solution chemistry (Johnson et al. 1999).

Soil solution samples collected from spruce-fir forests in GRSM have been shown to exhibit very high concentrations of NO_3^- and Al, compared with soil solution from similar forests in the northeastern United States (Joslin et al. 1992). At two study sites in GRSM, pulses of NO_3^- in soil solution caused Al^{3+} concentration to exceed levels known to impede root uptake of Ca^{2+} and Mg^{2+} by trees (Johnson et al. 1991b). The molar ratio of soil solution Ca:Al at these sites was consistently below 1.0, and often below 0.5. These values were identified by Cronan and Grigal (1995) as having 50% and 75% risk of adverse impact on tree growth, respectively.

Pardo et al (2007) modeled critical loads for acid deposition effects to forests in GRSM using ecological indicators of forest soil health, including soil BS, Al to base cation ratio, and Al concentration. The predicted critical loads at which the indicators were significantly impacted varied by forest type, but for most indicators the critical loads were exceeded by current deposition levels. Modeling of future deposition scenarios suggested that very large reductions of NO_x , SO_2 , and NH_3 , well beyond anything currently planned, would be needed to restore forest soil base status.

Soil acidification may also affect forest wildlife. For example, Hames et al (2002) found a strong negative effect of acidic deposition on the probability of breeding in birds. Low breeding success in the wood thrush, a species found in the Appalachians, was strongly correlated with low soil pH.

Acidification of Aquatic Ecosystems

The regions in the Southeast that were identified by Charles (1991) as containing large numbers of low-acid neutralizing capacity (ANC) surface waters were primarily the Appalachian Mountains in and around the APHN, the Mid-Atlantic Network, and northern Florida. The Appalachian Mountain region contains many streams that have low ANC, and the highest elevations of GRSM have received some of the highest rates of acidic deposition in the United States (Herlihy et al. 1993). Streamwater acid-base chemistry has been extensively studied in this region (e.g., Church et al. 1992, Herlihy et al. 1993, Sullivan et al. 2002a, 2003, van Sickle and Church 1995, Webb et al. 1994).

One of the most important processes affecting watershed acid-neutralization throughout much of the Southeast is S-adsorption on soil. If S adsorption on soil is high, relatively high levels of S deposition have little or no impact on stream acid-base chemistry, at least in the short-term. However, this S-adsorption capacity can become depleted over time under continued S deposition, and this causes a delayed acidification response. Sulfate mass balance analyses indicated that, because of watershed

SO₄²⁻ retention, soils and surface waters of the APHN region have not yet realized the full effects of elevated S deposition. Sulfur adsorption is relatively high in the soils of the Blue Ridge, where typically about half or more of the incoming S is retained (Herlihy et al. 1993). In general, S adsorption is higher in the southern portions of the Appalachian Mountain region, in and around GRSM. Herlihy et al. (1993) concluded that S retention will likely decrease in the future, resulting in further losses of stream ANC.

Acidic streams and streams with very low ANC in the APHN are almost all located in small (watershed area < 20 km²), upland, forested catchments in areas of base-poor bedrock. Acidic surface waters in this region are nearly always found in forested watersheds. The thin soils and steep slopes that make these watersheds unsuitable for agriculture and other development also contribute to their sensitivity to acidic deposition (Baker et al. 1990).

Localized studies have clearly shown that streamwater ANC is closely related to bedrock mineralogy in the APHN region (Herlihy et al. 1993). 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 µeq/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 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.

Elevations in GRSM are among the highest in the eastern United States, with the majority of the park land being higher than 1,000 m. Most streams in the park are first through third order (Sullivan et al. 2011b). Land slope tends to be fairly steep in GRSM, with most of the park having terrain steeper than 30°. In addition, some land along the Blue Ridge Parkway is steeper than 30°. Other parklands within the network generally have land slope less than 20°. These areas of steep terrain in GRSM and BLRI are generally considered to be more sensitive to acidification effects than are areas of relatively low relief. These low-order, high-elevation streams on steep terrain are often particularly sensitive to acidification impacts from both S and N deposition.

Cook et al. (1994) reported that high NO₃⁻ concentrations (~100 µeq/L) in upland streams in GRSM were correlated with elevation and forest stand age. The old-growth sites at higher elevation showed the highest NO₃⁻ concentrations. This pattern could have been due in part to the higher rates of N deposition and flashier hydrology at high elevation, and also decreased N uptake by trees in older forest stands. High N deposition has likely contributed to both chronic and episodic acidification of streamwater in the APHN (Flum and Nodvin 1995, Nodvin et al. 1995).

Model projections of future changes in acid-base chemistry of streams in the southeastern United States, including the APHN region, were reported by Sullivan et al. (2002a, 2003, 2005). They modeled future effects of atmospheric S and N deposition on aquatic resources in the eight-state

southern Appalachian Mountains region. Modeling was conducted with the MAGIC model for 40 to 50 sites within each of three physiographic provinces, stratified by streamwater ANC class. Simulations were based on assumed constant future atmospheric deposition at 1995 levels and on three regional strategies of emissions controls provided by the Southern Appalachian Mountains Initiative (SAMI), based on simulations performed with the Urban to Regional Multiscale One-Atmosphere model (Odman et al. 2002). The National Stream Survey statistical frame (Kaufmann et al. 1991) was used to estimate the number and percentage of stream reaches in the region that were projected to change their chemistry in response to the emissions control strategies. There was a small decline in the estimated length of projected acidic ($\text{ANC} \leq 0$) streams in 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 1995 levels.

The SAMI emissions control strategies used in the modeling reported by Sullivan et al. (2002a) 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 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 the acid rain controls under Title IV of the 1990 Amendments to the Clean Air Act, the 1-hour O_3 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 emissions control strategies. Some streams showed modeled stream water SO_4^{2-} concentrations increasing in the future, even while S deposition was reduced by more than two-thirds. These were mostly sites that had relatively low SO_4^{2-} concentrations in 1995 ($\leq$ about $50 \mu\text{eq/L}$) because of high 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 SO_4^{2-} 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 SO_4^{2-} ($> 50 \mu\text{eq/L}$) 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 SO_4^{2-} and NO_3^- 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. 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 of emissions controls would continue to accrue well beyond 2040 for all strategies, even if deposition was held constant at 2040 levels into the future (Sullivan et al. 2002a, 2004). Thus, recovery from past stream acidification is expected to be slow and gradual, even with rather large S emissions reductions.

Concentrations of NO_3^- in two streams in the Noland Divide watershed in GRSM decreased over the period 1991-1998 (Robinson et al. 2004). This trend was attributed to increased N uptake by understory vegetation growth that had been stimulated following the mortality of Fraser fir trees. Robinson et al. (2004) developed, based on monitoring data, multiple regression models for GRSM to predict stream ANC and concentrations and loads of various ionic constituents. Estimates did not differ depending on whether they were based on weekly to monthly sampling, thereby allowing the NPS to redirect resources from the ongoing weekly stream monitoring to other monitoring needs and to focus in the future on monthly monitoring. Despite reduced levels of acidic deposition in recent decades, Robinson et al. (2008) concluded that there has been little chemical recovery of acidified streams in GRSM.

Data from over 12,500 streams and lakes were used by the Critical Loads of Atmospheric Deposition Science Committee (CLAD) of the NADP (<http://nadp.sws.uiuc.edu/committees/clad/>) to develop steady-state critical loads (CL) for acidity of surface waters based on multiple approaches for estimating base cation weathering, including modified F-factors, regional regression model, and the dynamic Model of Acidification of Groundwater in Catchments (MAGIC). The water quality data were obtained from a variety of sources including EPA Long Term Monitoring (LTM) sites, lake surveys, EMAP Assessments, and National Stream Surveys; USGS; the NPS Vital Signs program; and the USFS air program. The average water quality measurements from the most recent five years of data were used for sites with long-term water monitoring records. Within the APHN, the CLAD database included CL estimates for 14 sites in BLRI and 16 sites in GRSM. Estimates were above 76 eq S/ha/yr for all modeled sites in these parks. Most sites studied in BLRI and GRSM (86% and 94%, respectively) had estimated CL above 259 eq S/ha/yr.

Geology, especially the presence of calcareous or pyritic bedrock, has substantial influence on stream chemistry in GRSM. The Anakeesta Formation contains pyrite, which weathers when exposed to the air by landslides and road cuts to produce sulfuric acid. It is exposed at many locations in the north-central portion of the park. In the western parts of GRSM, there are deposits of limestone and dolomite that provide substantial amounts of base cations to drainage water. Streams in GRSM that have $\text{ANC} > 100 \mu\text{eq/L}$ are mostly influenced by limestone weathering and are located mainly in the western portion of the park. Streams that have ANC near or below 0 $\mu\text{eq/L}$ are mostly influenced by Anakeesta weathering and are mainly located in the north-central portion of the park (Flum and

Nodvin 1995). Acidification in response to acidic deposition is superimposed on top of these spatial patterns in geology.

Temporal Variability in Water Chemistry

Temporal variability in surface water and soil solution chemistry, and patterns in nutrient uptake by terrestrial and aquatic biota, influence acidification processes and pathways. Conditions are constantly changing in response to episodic, seasonal, and inter-annual cycles and processes. Because of the steep topography and importance of S adsorption on soils in the APHN, episodic acidification of stream water is an important process. In particular, climatic fluctuations that govern the amount and timing of precipitation inputs, snowmelt, vegetative growth, depth to groundwater, and evapoconcentration of solutes influence soil and surface water chemistry and the interactions between pollution stress and sensitive aquatic and terrestrial biological receptors.

Chemical changes during hydrologic episodes are controlled in part by acidic deposition and in part by natural processes, including dilution of base cation concentrations, nitrification, flushing of organic acids from terrestrial to aquatic systems, and the neutral salt effect. Episodic acidification pulses may last for hours to weeks, and sometimes result in depletion of ANC in acid-sensitive streams to negative values, with concomitant increases in inorganic Al (Al_i) in solution, often to toxic levels.

During episodes, which are driven by rainstorms and/or snowmelt events, both discharge (streamflow volume per unit time) and water chemistry change, sometimes dramatically. This is important because streams may in some cases exhibit chronic chemistry that is suitable for aquatic biota, but nevertheless experience occasional episodic acidification with lethal consequences (cf., Wigington et al. 1993).

The most important factor governing watershed sensitivity to episodic acidification is the pathway followed by snowmelt water and stormflow water through the watershed. These pathways 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. All of these conditions occur at the high elevation locations in GRSM and along portions of BLRI.

Rainfall and snowmelt in GRSM typically pass through the soil profile prior to reaching a stream channel. The typical soil profile in acid-sensitive watersheds has lowest pH in upper organic soil horizons, increasing down the profile to higher pH at depth. Drainage water chemistry during baseflow conditions is generally reflective of conditions in the lower soil horizons and the subsoil. During high flows associated with snowmelt or rainfall events, however, 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). As such, storm flow and snowmelt are often associated with episodes of extreme 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).

Episodic acidification due to atmospheric deposition in GRSM has been associated in large part with N deposition, and effects are likely most pronounced during snowmelt. However, snowmelt can flush into surface waters N that was deposited from the atmosphere to the snowpack and also N that was mineralized within the soil under the snowpack during winter (Campbell et al. 1995). A substantial component of the NO_3^- flux may have been derived from mineralization of organic N (Ley et al. 2004). Episodic pH and ANC depressions in GRSM are driven by NO_3^- flux, base cation dilution, and pulses of increased SO_4^{2-} caused by S storage and release in soils.

Effects on Aquatic Biota

The southeastern United States is geologically diverse and was not glaciated during the most recent period of glaciation. As a consequence, a large number of aquatic animal species have evolved and colonized this region. Streams in the Tennessee-Cumberland aquatic region (Smith et al. 2002) are among the most biologically diverse in the world. This region contains the highest diversity of freshwater mussel and crayfish species and the highest levels of aquatic species endemism in North America (Abell et al. 2000, Smith et al. 2002), including, 231 species of fish (67 endemic), 125 species of mussels (20 endemic), and 65 species of crayfish (40 endemic). Regional habitat diversity and intraspecific genetic diversity are also regarded as high. Thus, the Southeast is a unique national biodiversity resource for fish and other aquatic organisms. More than 57 species of fish and 47 species of mussels are considered at risk (Abell et al. 2000, Master et al. 1998) due to a number of stressors, including acidification. The relative sensitivities of the various species are largely unknown.

It is likely that aquatic biota in the APHN have been affected by acidification at virtually all levels of the food web. Effects have been documented for fish and aquatic insects (Bulger et al. 1999, Cosby et al. 2006). 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. Surface water acidification typically results in the loss of the most acid-sensitive species first, and there is more loss with higher degrees of acidification, leading to decreasing overall species richness. In some cases, it is likely that all fish species have been eliminated from acidified streams.

Fish communities of high-gradient southern Appalachian streams may contain a variety of species, but are often dominated by trout, especially brook trout. Of the 15.1 million ha (37.4 million ac) in the southern Appalachian region (as defined by the Southern Appalachian Man and the Biosphere Program [1996]), 5.9 million ha (14.6 million ac [39%]) are in the range of native brook trout, with up to 53,000 km (33,000 mi) of potential native brook trout streams. 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. The highest-elevation fish species is usually brook trout, typically joined downstream by species of dace and darter, and perhaps by introduced brown (*Salmo trutta*) or rainbow (*Oncorhynchus mykiss*) 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 highly

acidified waters. Proceeding downstream, other dace, darters, chubs, shiners, suckers and others are often present. In larger downstream reaches, still regarded as high-gradient, the important gamefish smallmouth bass (*Micropterus dolomieu*) can be abundant (Wallace et al. 1992). Native brook trout inhabit about 970 km of stream length in GRSM, most of which is above 900 m elevation (Neff et al. 2009). The trout at higher elevation are more susceptible to acidification because of the lower pH typical of these streams.

In addition to stream chemistry, other factors are related to patterns of distribution and abundance of fish and other aquatic biota, especially temperature, gradient, stream order, and flow regime. Stream gradient can have substantial influence on water velocity, substrate size, number and size of pools, and oxygen content (Moyle and Cech 2000). All of these influence the habitat quality for aquatic biota.

Effects of stream acidity on benthic invertebrates were investigated by Rosemond et al. (1992) at four sites on Walker Camp Prong and its tributaries (Trout Branch and Cole Creek) in GRSM. Study sites exhibited similar physical stream characteristics, but differed in average baseflow pH from 4.5 to 6.4 due to varying influence of pyritic phyllite oxidation. The varying contributions of geologic acidity would be expected to mimic the effects of mineral acidity from acidic deposition. Species richness declined from 69 species at the highest pH site to 22 species at the lowest pH site. Richness of Ephemeroptera (mayflies) and Tricotera (caddisflies; both commonly acid-sensitive) was positively correlated with pH ($R^2 = 0.96$ for both). Tricotera species richness was negatively correlated with the concentration of Al_i ($R^2 = 0.96$). Differences in benthic invertebrate richness and density were not attributed to differences in food availability, but rather were closely associated with stream acid-base chemistry.

When exposed to low-pH, high-Al chemical conditions, fish can die or experience sublethal stress (Baldigo et al. 2007, MacAvoy and Bulger 2004). Acid stress in fish is commonly expressed as ion regulatory disturbance (Booth et al. 1988), interference with gill ion transport, and loss of blood sodium (Na^+ ; Grippo and Dunson 1996). Low concentrations of Ca^{2+} in water increase the vulnerability of fish to acid stress (Cleveland et al. 1991).

Neff et al. (2009) conducted *in situ* bioassays in GRSM to evaluate changes in physiological conditions and acid stress in wild southern strain brook trout during episodes of stream acidification. Stress was determined by measuring whole-body Na^+ loss (Grippo and Dunson 1996). Study streams were acidic (Eagle Rocks Prong) or very low in ANC ($< 20 \mu eq/L$; Middle Prong, Ramsey Prong; Deyton et al. 2008). Two of the streams had lost brook trout populations during the past two decades. Episodic ANC depressions that occurred during the bioassay exposure experiments ranged from 9 to $26 \mu eq/L$. The main contributor to episodic acidification was SO_4^{2-} ; NO_3^- , organic acids, and base cation dilution also contributed.

During episodes, brook trout lost Na^+ in a manner consistent with stress caused by acidification. Whole-body Na^+ concentrations decreased by significant amounts (10-19% loss) when the 24-hr time-weighted average Al concentration exceeded $200 \mu g/L$ ($7.4 \mu M$) and pH was less than 5.1. Loss of Na^+ can cause or contribute to mortality (Hesthagen et al. 1999) or sublethal stress (Dussault et al.

2005), stimulate downstream immigration (Gagen et al. 1994), interfere with reproduction (Kaesler and Sharpe 2001), and reduce growth (Cleveland et al. 1991).

Nutrient Enrichment

The network rankings for nutrient N Pollutant Exposure, Ecosystem Sensitivity to nutrient enrichment, and Park Protection reported by Sullivan et al. (2011a) in a coarse screening assessment yielded an overall Network Risk ranking for the APHN that was in the second highest quintile among all networks (Sullivan et al. 2011a). The overall level of concern for nutrient N enrichment effects on I&M parks within this network was considered High by 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.

Estimated nutrient N Pollutant Exposure rankings calculated by Sullivan et al. (2011a) for individual I&M parks within the APHN were High for all parks in the network (Table 3). However, as was indicated for the acid Pollutant Exposure ranking (Table 2), the nutrient N Pollutant Exposure ranking for GRSM and at high elevation locations in BLRI is likely biased low because unmeasured cloud deposition of N can be substantial at the very high-elevation locations that predominate in those parks.

Table 3. 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 Enrichment
<i>Big South Fork</i>	BISO	High	Very Low
<i>Blue Ridge Parkway</i>	BLRI	High	Moderate
<i>Great Smoky Mountains</i>	GRSM	High	Very Low
Obed	OBRI	High	Very Low

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.

Sullivan et al. (2011a) estimated that resources in the individual parks in the APHN may not be as sensitive to nutrient enrichment effects from atmospheric N deposition as parks in some other networks. High-elevation lakes might be more prone than lakes at lower elevation to N-limitation, and therefore are considered potentially more susceptible to eutrophication in response to atmospheric N input. Elevations in GRSM are among the highest in the eastern United States, with the majority of the park lands being higher than 1,000 m elevation. There are reservoirs along the boundary of GRSM, but they are generally not located at high elevation, and are therefore not considered to be especially sensitive to nutrient enrichment impacts. The parks in the APHN also generally lack the vegetation types thought to be most sensitive to nutrient N enrichment impacts. The latter include wetlands, arid, and semi-arid plant communities.

Nitrogen deposition poses a potential for nutrient enrichment to temperate forest ecosystems because the growth of trees in these systems is often N-limited (Vitousek and Howarth 1991). Forest canopy

structure can enhance rates of N deposition to terrestrial ecosystems by scavenging dry N deposition from the atmosphere (Lovett 1992). Forests considered sensitive to N deposition include high-elevation forests which receive high rates of N deposition, and where effects of N deposition on root allocation or late-season growth may exacerbate other stresses from acidic deposition and harsh climate. The effects of excess N on sensitive forests can be exacerbated in forests that have already experienced soil base cation depletion due to the acidifying effects of acidic deposition.

In some areas, particularly in high-elevation terrestrial ecosystems which have become N-saturated, high levels of atmospheric N deposition have caused elevated levels of NO_3^- in drainage waters, making these areas potentially more sensitive to added N deposition (Aber et al. 1989, Aber et al. 1998, Bowman et al. 2006, Campbell et al. 2002, Stoddard 1994). Elevated NO_3^- leaching contributes to depletion of base cations from forest soils, causing adverse effects on sensitive tree species and acidification of drainage waters in base-poor soils (Aber et al. 1989, Aber et al. 1998, Stoddard 1994). In general, sites receiving high N deposition also are subject to other pollutant exposures, including O_3 .

There is concern that atmospheric N deposition at GRSM has exceeded biological demand for N, and that excess N will reduce forest growth due to increased frost damage (Friedland et al. 1984) and enhance NO_3^- leaching, thereby causing nutrient base cation deficiencies and Al mobilization. Stream water quality might be also adversely affected (Stoddard 1994).

The status of red spruce in GRSM is of concern, with evidence for radial growth decline during the previous century at some locations (McLaughlin et al. 1987, Webster et al. 2004). The Blue Ridge Parkway also has small quantities of spruce/fir forest. The highest point on the Parkway is a spruce/fir stand. The nature of the relationship between climate, acidic deposition, and red spruce growth in and near the APHN is complex (Webster et al. 2004). Trees near ridges showed earlier, faster, and more consistent declines in growth than did trees in draws at lower elevation, likely due to both climatic conditions and acidic and nutrient N deposition (Webster et al. 2004). The authors proposed a conceptual model, supported by field data, to explain the growth differences as follows. Red spruce trees experience more extreme climatic conditions near the ridges due to orographic precipitation, frequent cloud emersion, and enhanced S and N deposition (Lindberg and Owens 1993, Mohnen 1992). The cloud base recorded during the Integrated Forest Study at GRSM was generally at about 1800 m elevation (Johnson and Lindberg 1992), well within the range of many ridge tops in the park. Soils along ridges in GRSM tend to be shallow, often < 50 cm, compared to deeper soils downslope (Johnson et al. 1991b). Ridge soils also tend to be less stable, leading to more frequent landslides and transfer via erosion of soil (with associated base cations) to lower elevation positions (Fernandez 1992, White and Cogbill 1992). Soil pools of exchangeable Ca and Mg, and associated BS, are small in response to the higher precipitation, enhanced leaching, and shallow depth at the higher elevation locations (Johnson and Fernandez 1992). Shallow soils having low base cation supply may lack the capacity to provide sufficient nutrient cations needed for tree growth (Webster et al. 2004). In contrast, the deeper, more base-rich soils in the mountain draws experienced a transient enrichment of base cations in soil solution transported from upslope locations and a delayed negative growth response to acidifying deposition.

Garten et al. (1994) demonstrated that naturally occurring N isotope ratios in plant foliage can provide a good index of soil N dynamics in GRSM at sites ranging in elevation from 615 to 1670 m in different forest types. Soils and organic layers from the N-rich high-elevation locations showed greater net N mineralization and nitrification potentials than soils from lower-elevation locations, making them more prone to N saturation. The spruce-fir forests in GRSM appear to be N-saturated. This could contribute to adverse effects on forest health. Nevertheless, red spruce has not shown widespread mortality that might be attributed to acidification (Busing and Wu 1990, Nicholas et al. 1992, Pauley et al. 1996, Peart et al. 1992). There has been some loss of foliage, and secondary wind damage has occurred due to opening of the canopy in response to insect-caused fir mortality (Busing and Pauley 1994). There are complex relationships among insect infestation, wind disturbance, acidic deposition, and nutrient cycling that are not well understood (Pauley et al. 1996).

High-elevation spruce-fir forests in GRSM have been found to lose about 10-20 kg N/ha/yr to NO_3^- leaching (Johnson et al. 1993a). This high NO_3^- leaching reflects high soil N availability and N saturation (Aber et al. 1989, Agren and Bosatta 1988). High atmospheric N deposition, high rate of net nitrification, and low biological demand for N in these primarily old-growth forests further contribute to NO_3^- leaching (Sasser and Binkley 1989, Van Miegroet et al. 1992).

High-elevation spruce-fir forests in GRSM have for the most part not been logged or burned extensively (Harmon et al. 1983, Pyle 1988). As a consequence, soil N pools in spruce-dominated stands tend to be large and the N mineralization potential is high (Garten 2000, Van Miegroet et al. 1992). Because of the high rate of N deposition to high-elevation spruce-fir forests in GRSM, these forests are set on a path to N saturation. The rate of change and the time at which the forest becomes N saturated are influenced by stand vigor, tree age, and disturbance (Creed et al. 2004). Streams in GRSM have among the highest NO_3^- concentrations in the eastern United States (Stoddard 1994), and this is symptomatic of advanced N saturation.

The extensive mortality of Fraser fir (Pauley et al. 1996) has had a large impact on the quantity of coarse woody debris (CWD) in these forests. An estimated 70% of the standing Fraser fir trees in the Noland Divide watershed were dead at the end of the 20th Century due to the balsam wooly-adelgid, an exotic insect pest (Rose 2000). Creed et al. (2004) investigated the role of CWD as a source or sink of N in the stream ecosystems that drain these forests. As an N sink, CWD can help to mitigate N leaching; as an N source, it can amplify N export from the watershed. Creed et al. (2004) found evidence of large changes in N content of CWD, with N dynamics changing over decadal time scales.

Barker et al. (2002) estimated spatial variability in tree N uptake in the Noland Divide watershed in GRSM and assessed the influence of stand and landscape characteristics on forest N uptake. They found that overstory N uptake was highly variable spatially within the small study watershed and depended in large part on the methods used to calculate uptake. It appeared that the overstory component of this high-elevation spruce-fir forest played only a minor role in the retention of atmospherically deposited N (Barker et al. 2002). Van Miegroet et al. (2001) investigated the magnitude and timing of N fluxes in a small, first-order stream catchment in GRSM. Approximately half of the atmospheric N input was exported in stream water annually. Asynchrony was found for

the N inputs and outputs, however. Atmospheric deposition was highest during summer, whereas NO_3^- leaching losses were largest during the dormant winter season.

Foliar N concentration in American beech (*Fagus grandifolia*), sugar maple, and yellow birch (*Betula alleghaniensis*) increased along an N deposition gradient across North Carolina and Virginia from about 9 to 15 kg N/ha/yr (Boggs et al. 2005). In a separate study across North Carolina and West Virginia, Brookshire et al. (2007) documented increased stream NO_3^- concentrations with increasing N deposition ranging from 5 to 32 kg N/ha/yr. Such high levels of N deposition occur in GRSM, and to a lesser degree in the southern sections of BLRI.

Stream NO_3^- concentration in GRSM tends to be high at watersheds that receive especially high N deposition (> 32 kg N/ha/yr; Pardo and Duarte 2007, Weathers et al. 2006). The CL for nutrient N addition to forest ecosystems in GRSM has been estimated using the steady state mass balance (SMB) modeling approach to range from about 2.5 to 9 kg N/ha/yr by Oja and Arp (1998) and from 3 to 7 kg N/ha/yr by Pardo and Duarte (2007). Gilliam et al. (2011) compiled data on empirical N CLs for the Eastern Temperate Forests ecoregion. For GRSM, they estimated a CL of 32 kg N/ha/yr to protect against export of N in stream water. This estimate was based on stream chemistry published by Garten (2000) and Van Miegroet et al. (2001), combined with N deposition estimates of Pardo and Duarte (2007) and Weathers et al. (2006).

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. 2011). Ellis et al. (2013) estimated the N CL for GRSM in the range of 3-8 kg N/ha/yr for protection of hardwood forests.

Ozone Injury to Vegetation

Ozone Formation

Sources of air pollution that are hundreds of miles from parks in the APHN may be linked to O₃ exposure at the parks. In particular, these include emissions sources in the Ohio Valley and the Gulf of Mexico regions (Tong et al. 2005). The highest O₃ exposures in GRSM occur on hot, sunny days having low wind speed, contributing to air stagnation (Tong et al. 2005).

There are recognized differences in the potential to form atmospheric O₃ among the prominent southeastern national parks, including GRSM (Kang et al. 2003). Tong et al. (2005) quantified the relative importance of point and nonpoint mobile emissions sources of N oxides, identified the origin of air masses associated with high concentrations of N oxides, and calculated N oxide production and removal budgets for two national parks (GRSM and MACA). Air pollution influence areas were identified using cluster analysis (Dorling et al. 1992) of model output generated using the Hybrid Single-Particle Lagrangian Integrated Trajectories (HYSPLIT) model (Draxler 1997) and also emission source identification based on EPA's national emissions inventory (U.S. EPA 2001b). Clusters were labeled according to general direction of movement of the air mass towards the parks.

Diurnal reactive N oxide (NO_y) and SO₂ patterns were identified by Tong et al. (2005) for GRSM, with weak maxima during early morning and minima during late afternoon throughout most of the year. The proportion of NO_y emissions derived from point sources was generally higher during winter and spring, and lower during summer and fall.

It is believed that NO_y, rather than VOC, is the main limiting factor for photochemical O₃ production in remote areas of the southeastern United States such as within the APHN (Kang et al. 2003, Tong et al. 2005). On average, a minimum of one-fourth of reactive N oxides at GRSM are estimated to have been emitted by point sources of N (Tong et al. 2005). GRSM also has strong biogenic (emitted from natural vegetation) VOC sources. The most abundant VOC compound measured in the air during summer in GRSM during the period 1995-1997 was isoprene (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 69-95% of the total atmospheric VOC concentration in GRSM during all three years of study. Most 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).

Episodes of high (> 90 ppb) O₃ concentrations in GRSM were primarily attributed to atmospheric transport of O₃ into the park from outside rather than formation of O₃ within the park (Mueller 1994). Mueller et al. (1996) characterized four episodes of high ambient O₃ concentrations (having 1-hr average O₃ concentration > 90 ppb) at GRSM. Based on model simulations and detailed episode analysis, the researchers concluded that urban pollution sources of NO_y were likely to play a large role in determining episodes of high O₃ concentrations in GRSM.

Kang et al. (2003) applied the Multiscale Air Quality Simulation Platform (MAQSIP) model to predict atmospheric O₃ concentration with an overall uncertainty less than 30% in GRSM and in two national parks in surrounding networks. Modeling results suggested that VOCs were chemically saturated at all three locations, potentially causing decreased O₃ production in response to further increases in VOC emissions. More than half of the O₃ at GRSM was simulated to be transported from other areas (Kang et al. 2003). The authors concluded that, in areas like GRSM 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).

NPS (2010) evaluated the fourth-highest 8-hour O₃ concentrations for national parks that have consistently been at or above the primary (human health level) National Ambient Air Quality Standard (NAAQS), based on 11-20 years of monitoring data running through 2008. There were six parks that routinely had such high concentrations, including GRSM. This park experienced the most rapid rise since the 1990s among eastern national parks in the frequency of occurrence of days during which an 8-hr average O₃ concentration exceeded the standard (Tong et al. 2005).

Ozone Sensitive Plants

GRSM is one of the most diverse national parks for vascular plants (Shaver et al. 1994). This park also contains more than half of all old-growth forest in the eastern United States and more than three-fourths of the spruce-fir forest in the southern Appalachian Mountains (Burkey et al. 2006). Thus, threats to vegetation in this park are of regional and national importance (Shaver et al. 1994).

The O₃-sensitive plant species that are known or expected to occur within the I&M parks found in the APHN are listed in Table 4. Those considered to be bioindicators display visible and easily recognizable O₃ injury symptoms. They are designated by an asterisk in the table. Each park within the network contains a number of O₃ sensitive and bioindicator species. In addition to causing visible injury (necrosis, stippling), O₃ can reduce photosynthesis and growth. Effects are usually induced by cumulative exposures over time; cumulative exposures are expressed as the W126 or the SUM06 metrics, which are calculated by summing up hourly O₃ concentrations over a period of time, usually 3 months during the growing season.

Ozone Exposure Indices and Levels

The southern Appalachian Mountains region has experienced some of the highest O₃ concentrations of any physiographic area in the eastern United States (Chappelka et al. 1997, Grulke et al. 2007, Samuelson and Kelly 1997). Visible foliar symptoms suggestive of foliar injury have been observed on over 90 plant species in GRSM, many of which were verified in open-top chamber exposures (Neufeld et al. 1992).

The W126 (a measure of cumulative O₃ exposure that preferentially weights higher concentrations) and SUM06 (a measure of cumulative exposure that includes only hourly concentrations over 60 ppb O₃) exposure indices calculated by NPS staff are given in Table 5, along with Kohut's (2007a) O₃ risk ranking. The two ranking systems differ. The NPS (2010) ranking system ranks O₃ exposure levels according to injury thresholds from the literature (Heck and Cowling 1997). Kohut's rankings consider both O₃ exposure and soil moisture. 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 the O₃ season (summer), O₃ uptake and injury are limited by stomatal closure even when O₃ exposures are relatively high. Thus, although O₃ conditions are rated as Moderate by NPS in BLRI, for example, Kohut concluded that the risk to vegetation is Low in BLRI because of generally dry soil conditions during the summer. In contrast, vegetation in BISO, GRSM, and OBRI is rated at High risk.

Table 4. Ozone sensitive and bioindicator plant species known or thought to occur in the I&M parks of the Appalachian Highlands Network. (Data Source: E. Porter, National Park Service, pers. comm., August 30, 2012; lists are periodically updated and available at <https://irma.nps.gov/NPSpecies/Report>)

Species	Common Name	Park ¹			
		<i>BISO</i>	<i>BLRI</i>	<i>GRSM</i>	<i>OBRI</i>
<i>Aesculus flava</i>	Yellow buckeye			x	x
<i>Ageratina altissima</i> *	White snakeroot		x		
<i>Ailanthus altissima</i> *	Tree-of-heaven	x	x	x	x
<i>Apios americana</i> *	Groundnut	x	x	x	
<i>Apocynum androsaemifolium</i> *	Spreading dogbane		x	x	
<i>Apocynum cannabinum</i>	Dogbane, Indian hemp	x	x	x	
<i>Artemisia ludoviciana</i> spp. <i>Mexicana</i> *	Silver wormwood			x	
<i>Asclepias exaltata</i> *	Tall milkweed	x	x	x	x
<i>Asclepias incarnata</i>	Swamp milkweed		x		
<i>Asclepias incarnata</i> spp. <i>pulchra</i>	Swamp milkweed			x	
<i>Asclepias syriaca</i> *	Common milkweed	x	x	x	
<i>Cercis canadensis</i> *	Redbud	x	x	x	x
<i>Clematis virginiana</i>	Virgin's bower	x	x	x	x
<i>Corylus americana</i> *	American hazelnut	x	x	x	x
<i>Eurybia macrophylla</i> *	Big-leaf aster	x	x	x	
<i>Fraxinus americana</i> *	White ash	x	x	x	x
<i>Fraxinus pennsylvanica</i>	Green ash	x	x	x	
<i>Gaylussacia baccata</i> *	Black huckleberry	x	x	x	x
<i>Krigia montana</i>	Mountain dandelion		x	x	
<i>Liquidambar styraciflua</i>	Sweetgum	x		x	x
<i>Liriodendron tulipifera</i> *	Yellow-poplar	x	x	x	x
<i>Lyonia ligustrina</i> *	Maleberry	x	x	x	x
<i>Oclemena acuminata</i> *	Whorled aster		x	x	
<i>Parthenocissus quinquefolia</i>	Virginia creeper	x	x	x	x
<i>Pinus pungens</i>	Table-mountain pine		x	x	
<i>Pinus rigida</i>	Pitch pine	x	x	x	
<i>Pinus taeda</i>	Loblolly pine			x	x

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

* Bioindicator species

Table 4 (continued). Ozone sensitive and bioindicator plant species known or thought to occur in the I&M parks of the Appalachian Highlands Network. (Data Source: E. Porter, National Park Service, pers. comm., August 30, 2012; lists are periodically updated and available at <https://irma.nps.gov/NPSpecies/Report>)

Species	Common Name	Park ¹			
<i>Pinus virginiana</i>	Virginia pine	x	x	x	x
<i>Platanus occidentalis</i> *	American sycamore	x	x	x	x
<i>Populus tremuloides</i> *	Quaking aspen		x		
<i>Prunus serotina</i> *	Black cherry	x	x	x	
<i>Prunus virginiana</i>	Choke cherry		x	x	
<i>Rhus copallinum</i>	Winged sumac	x	x		x
<i>Robinia pseudoacacia</i>	Black locust	x	x	x	x
<i>Rubus allegheniensis</i> *	Allegheny blackberry	x	x	x	x
<i>Rubus canadensis</i> *	Thornless blackberry		x	x	
<i>Rubus cuneifolius</i>	Sand blackberry	x			
<i>Rudbeckia laciniata</i> var. <i>humilis</i> *	Cutleaf coneflower			x	
<i>Rudbeckia laciniata</i> *	Cutleaf coneflower	x	x		x
<i>Sambucus canadensis</i> *	American elder	x	x		x
<i>Sambucus racemosa</i> *	Red elderberry		x		
<i>Sassafras albidum</i>	Sassafras	x	x	x	x
<i>Solidago altissima</i>	Goldenrod	x	x		
<i>Verbesina occidentalis</i> *	Crownbeard	x	x	x	x
<i>Vitis labrusca</i> *	Northern fox grape	x	x	x	x

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

* Bioindicator species

Table 5. NPS ozone conditions and risk to vegetation for I&M parks in the APHN. NPS condition is based on estimated 3-month W126 and SUM06 ozone exposure indices for the period 2005-2009. Risk to vegetation is based on several factors that contribute to injury in plants, including ozone exposure and environmental variables¹.

Park Name ¹	Park Code	W126		SUM06		Risk to Vegetation
		Value (ppm-hr)	NPS Condition	Value (ppm-hr)	NPS Condition	
<i>Big South Fork</i>	BISO	12.79	Moderate	16.98	High	High
<i>Blue Ridge Parkway</i>	BLRI	11.39	Moderate	14.97	Moderate	Low
<i>Great Smoky Mountains</i>	GRSM	12.38	Moderate	16.78	High	High
Obed Wild and Scenic River	OBRI	14.41	High	19.38	High	High

¹ Parks are classified into one of three ranks (Low, Moderate, High).

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

Both the SUM06 and W126-3 mo indices at OBRI exceeded O₃ exposure levels considered necessary for causing foliar injury (Kohut 2007b). In general, soil moisture was low when O₃

concentration was high, but this pattern was not consistent. Thus, the risk of O₃ injury to foliage was high in this park, but dry soil conditions might reduce the likelihood of foliar injury. The SUM06 index significantly exceeded the threshold for foliar injury at all four monitoring sites in GRSM (Lookout Rock, Cade's Cove, Cove Mountain, and Clingmans Dome) during the period 1995-1999. In addition, the numbers of hours having O₃ concentrations above 100 ppb often met the threshold for injury for the W126 criterion (Kohut 2007b). The highest exposures generally occurred at the Lookout Rock ridge site and the Cove Mountain high-elevation site. In general, when O₃ was high, soil moisture was low at both locations, thereby reducing the effectiveness of O₃ in causing foliar injury. The probability of foliar symptoms in GRSM is likely highest when O₃ levels exceed thresholds and soil moisture levels are normal (e.g., 1997, 1999) or at least high enough that O₃ uptake into foliage is not constrained by stomatal closure (Kohut 2007b).

Kohut (2007b) found that the cumulative number of ppm-hours of exposure in BISO exceeded the estimated threshold for foliar symptoms during the period 1995-1999. Soil moisture levels were also high enough to favor the uptake of O₃ into leaf tissues. However, in general, soil moisture levels and atmospheric O₃ concentrations were inversely related: when O₃ was high, soil moisture was low. Thus, the effectiveness of the O₃ exposure in producing foliar injury was reduced. The probability of foliar injury may be greatest during years when soil moisture is normal (absence of drought) and O₃ concentrations are moderately high (e.g., 1996), and during years when drought occurs late in the growing season and O₃ exposures are high (e.g., 1998; Kohut 2007b).

During the period 1995-1999, Kohut (2007b) found that, although there were numerous O₃-sensitive plant species at BLRI, atmospheric O₃ levels were not high enough to expect foliar symptoms. The SUM06 exposure threshold was generally satisfied, but the W126 criteria were not. Concentrations of O₃ above 100 ppb were rare, and moisture conditions constraining O₃ foliar uptake occurred across the range of O₃ exposures that were found.

During the last two decades of the 20th century, ground-level O₃ concentrations in the United States generally decreased about 21% and 12%, based on the previous 1-hour standard and the newer 8-hour standard, respectively (U.S. EPA 2001a). Nevertheless, O₃ concentrations did not decrease in all regions. In the southern and north central regions, O₃ concentrations generally increased. Seasonal O₃ exposure increased dramatically in GRSM between 1990 and 1999 (Chappelka et al. 2003). However, between 2000 and 2009, both O₃ concentrations and O₃ exposures decreased at GRSM.

The EPA's proposal in 2010 for a new secondary O₃ standard to protect vegetation was based on a three-year average of the annual W126-3 month metric (Federal Register Vol. 75, No. 11, 40 CFR Parts 50 and 59, January 2010), and identified a possible range for the new standard as 7-15 ppm-hr. There were 17 parks that exceeded the upper end of this range in 2008. The eastern park showing the highest exposure was GRSM (22 ppm-hr). EPA decided not to set a plant-based standard, but retained the human health-based standard of 75 ppb, averaged over eight hours. Even though there have been widespread improvements in atmospheric O₃ levels there were still 51 monitoring locations classified as nonattainment areas in 2007 because of failure to meet the O₃ NAAQ standard (U.S. EPA 2008b). Some of the highest O₃ concentrations in the United States in 2007 were located in Georgia and North Carolina (U.S. EPA 2008b).

Field Surveys

An intensive O₃ effects research effort has been conducted at GRSM since the early 1990s, including field surveys, chamber fumigations, and routine monitoring (Shaver et al. 1994). These studies revealed foliar injury and adverse physiological effects of O₃ on vegetation in the park at O₃ concentrations lower than the previous NAAQS of 120 ppb (Shaver et al. 1994). Some plant species and populations showed adverse effects on plant growth at ambient O₃ exposure levels when compared with plants placed in chambers receiving charcoal-filtered air (Neufeld and Renfro 1993a).

Somers et al. (1998) quantified differences in radial growth of black cherry (*Prunus serotina*) and yellow poplar (*Liriodendron tulipifera*) among individual trees in GRSM with and without histories of visible foliar symptoms from O₃ exposure. Radial growth decreased over both 5- and 10-year periods of measurement for both species, but these decreases were only statistically significant ($p \leq 0.05$) for yellow poplar. This study provided empirical evidence, at least for yellow poplar, that visible O₃ symptoms are related to growth decline of individual trees growing in a natural setting. Experiments conducted in GRSM further identified black cherry and American sycamore (*Platanus occidentalis*) trees as having foliar symptoms caused by O₃ (Neufeld and Renfro 1993a, b). Foliar injury due to O₃ exposure was documented by Chappelka et al. (1999a) on mature black cherry in GRSM. Trees growing at the highest elevations showed the greatest 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.

A three-year study in the early 1990s at three locations in GRSM showed that about 11 to 12% of all leaves examined of black cherry, sassafras, and yellow poplar showed visible O₃ symptoms. Ozone symptoms in the park were greatest at the Cove Mountain site during all three years of study, with less visible symptoms at Look Rock and Twin Creeks (Chappelka et al. 1999b). During the period 1992 to 1996, the average incidence of O₃-induced foliar symptoms on milkweed in GRSM was 73% (Chappelka et al. 2007). Ozone symptoms can also vary with age of leaves. For example, symptoms on tall milkweed (*Asclepias exaltata*) in GRSM were most severe in older, lower leaves which had been exposed to O₃ for a longer period of time (Souza et al. 2006).

Cutleaf coneflower showed substantial variation in symptoms of O₃ injury between and within populations in GRSM. Research reported by Davison et al. (2003) suggested that variation in symptom expression was likely due to variation in light, and not to variation in O₃ flux. This finding reinforces the importance of evaluation of environmental site conditions in determining visible symptom expression from air pollution injury.

During July and August of most summers, about 25 to 30 plant species in GRSM develop foliar symptoms of O₃ injury (Finkelstein et al. 2004). Cutleaf coneflower is common throughout GRSM at the boundary between forest and meadow. Stands range from about 1-20 m wide and can run along the forest edge for hundreds of meters (Finkelstein et al. 2004). Roughly half of the plants of this species in GRSM typically show visible symptoms of foliar injury (Finkelstein et al. 2004).

Trees in GRSM exhibited reduced growth and increased water loss in years that had highest O₃ exposure (McLaughlin et al. 2007a). The increased water loss from trees contributed to reduced soil moisture and decreased fall-season stream flow (McLaughlin et al. 2007b).

Chappelka et al. (1996) conducted an O₃ effects assessment for the southern Appalachian Mountains. They found it difficult to rank tree species' sensitivities to O₃ injury because of high variability across the study region in environmental conditions, O₃ exposure, tree age, and differential sensitivity within a given species. Of the five tree species most studied, however, black cherry and loblolly pine appeared most sensitive and red spruce least sensitive; yellow poplar and northern red oak were judged to be intermediate in sensitivity.

Samuelson and Kelly (1997) characterized foliar O₃ uptake in forest trees of three different sizes (seedling, sapling, mature tree) in GRSM. Light-saturated net photosynthesis, stomatal conductance, and O₃ uptake were measured in black cherry, northern red oak (*Quercus rubra*), and red maple (*Acer rubrum*) over two growing seasons at high and low elevation. Seasonal O₃ dose (i.e., uptake into the leaf) to black cherry was up to six times higher in mature black cherry trees compared to seedlings and saplings of the same species. Differences for northern red oak and red maple were 50% less.

There is evidence (cf., McLaughlin et al. 2007b) that O₃ can contribute to reduced stream baseflow during fall low-flow periods in the APHN. In response to O₃ exposure, there was increased forest water use, perhaps due to increased evapotranspiration, and reduced fall season baseflows in all three watersheds examined near Look Rock, 15 km southeast of GRSM. Such changes in streamflow during the critical low-flow period could have substantial effects on water quality and stream ecology, especially in small, low-order streams. Model results further suggested that the cumulative effects of daily peak O₃ exposures appeared to be more important than longer-term averages at the scale of the individual tree and the small watershed. Thus, McLaughlin et al. (2007b) suggested that O₃ exposure can magnify the effects of drought and exacerbate the effects of climate warming.

McLaughlin et al. (2007a) found growth effects on mature forest trees at three study sites in and near GRSM. Manual measures of stem circumference of 86 trees were recorded at approximately two-week intervals and were linked to electromechanical radius measurements at 30-minute intervals for 6 trees. The manual measures were of gap changes on tensioned bands and were obtained with digital calipers to an average precision of 0.02 mm. High resolution radius measures were made with electromechanical dendrometers (sensitivity = 0.006 mm radius change). Stem growth reductions were accompanied by changes in water use by trees. The authors concluded that altered water use could further affect tree growth during drought years, and that O₃ exposure at the study locations increased water use on an episodic basis and limited tree growth. Episodic increases in O₃ exposure during the growing season corresponded with reduced stem increment. Thus, it appears that peak O₃ exposure can play a role in regulating water loss from trees via transpiration and can delay the recovery of stem expansion subsequent to episodes of high moisture demand (McLaughlin et al. 2007a).

Model Responses

Weinstein et al. (2001) used the tree physiology model, TREGRO, linked to the stand simulation model, ZELIG, to estimate the effects of O₃ exposure on yellow poplar forest in the Twin Creeks region of GRSM. Ambient O₃ levels measured at low elevation on the west side of GRSM were predicted to cause a 10% reduction in yellow poplar abundance over the next century. Reduction of O₃ exposure by 50% was projected to be insufficient to prevent a decrease in future tree abundance.

Visibility Degradation

Natural Background and Ambient Visibility Conditions

Visibility is a key air quality indicator. Air pollution can cause haze and reduce visibility, affecting how far and how well we can see. NPS management policies prohibit impairment of visibility in all national park units. 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 visibility 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. Natural background visibility assumes no human-caused pollution, but varies with natural processes such as windblown dust, fire, volcanic activity and biogenic emissions. Visibility is monitored by the Interagency Monitoring of Protected Visual Environments (IMPROVE) network and typically reported using the haze index deciview¹ (dv).

Current visibility estimates reflect current pollution levels, and also include natural background conditions, that is, conditions that would exist in the absence of human-caused pollution. Estimates 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 IMPROVE monitors were used in generating the visibility ranking. Table 6 gives the relative park haze rankings on clearest, haziest, and average days. NPS ARD uses interpolated estimates of average visibility to assess condition at all parks. Visibility conditions were rated as warranting significant concern at all APHN parks for the period 2005-2009 (NPS-ARD In preparation).

Natural background estimates of haze are relatively high in the region, due to biogenic emissions. However, measured ambient haze for the period 2004 through 2008 was considerably higher than the estimated natural condition. Ambient haze was classified as Very High for all visibility days. For example, haze for the average day was more than 13 dv higher than the estimated average natural haze. On the haziest 20% of days, ambient haze was more than 18 dv higher than the estimated natural condition. A report from the U.S. EPA (2008a) on the status and trends in air quality throughout the United States concluded that visibility in GRSM on the 20% haziest days during the period 2000 to 2004 (30.3 dv) was among the poorest in the country.

¹ 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.

Table 6. Estimated natural haze and measured ambient haze in I&M parks averaged over the period 2004 through 2008¹.

Park Name ²	Park Code	Site ID	Estimated Natural Background Haze (dv)					
			20% Clearest Days		20% Haziest Days		Average Days	
<i>Big South Fork</i>	BISO	No Site						
<i>Blue Ridge Parkway</i>	BLRI	No Site						
<i>Great Smoky Mountains</i>	GRSM	GRSM1	4.62		11.24		7.73	
Obed	OBRI	No Site						
Park Name	Park Code	Site ID	Measured Ambient Haze (For Years 2004 through 2008)					
			20% Clearest Days		20% Haziest Days		Average Days	
			dv	Ranking	dv	Ranking	dv	Ranking
<i>Big South Fork</i>	BISO	No Site						
<i>Blue Ridge Parkway</i>	BLRI	No Site						
<i>Great Smoky Mountains</i>	GRSM	GRSM1	13.09	Very High	29.79	Very High	21.18	Very High
Obed	OBRI	No Site						

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

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

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, promulgated in 1999, 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 estimation of baseline visibility conditions, calculation of the glide slope from the baseline necessary to achieve background conditions in 2064, and determination of air pollutant source areas.

Three representative photos are shown in Figure 1 of the same vista in GRSM under differing visibility conditions. 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 from GRSM show that pollution has reduced average natural visual range from 110 miles to 25 miles. On the haziest days, visual range is reduced from 75 to 10 miles. Severe haze episodes occasionally reduce visibility to 6 miles.

Great Smoky Mountains

20% Clearest Days

Taken: 9:00 AM

Haze = 13 dv

$B_{\text{ext}} = 36 \text{ Mm}^{-1}$

VR=110 km



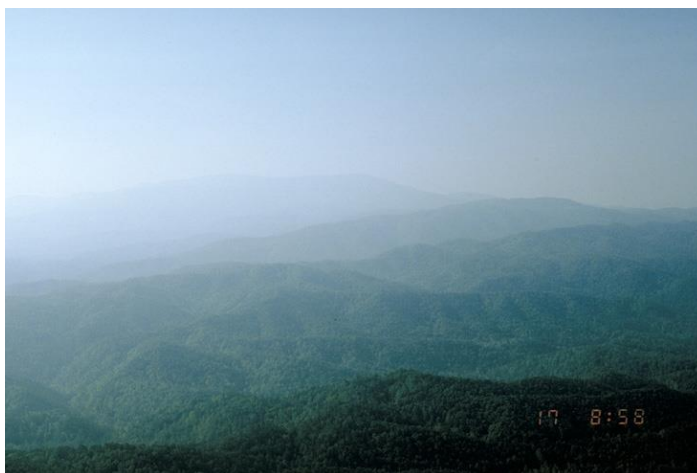
20% Haziest Days

Taken = 9:00 AM

Haze = 28 dv

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

VR = 25 km



Average Days

Taken = 9:00 AM

Haze = 23 dv

$B_{\text{ext}} = 98 \text{ Mm}^{-1}$

VR = 40 km



Figure 1. Three representative photos of the same view in GRSM illustrating the 20% clearest visibility days, the 20% haziest visibility days, and the annual average visibility. B_{ext} is total particulate light extinction; VR is visibility range.

Composition of Haze

Various pollutants make up the haze that causes visibility degradation. IMPROVE measures these pollutants and reports them as ammonium sulfate, ammonium nitrate, elemental carbon, coarse mass, organic mass, sea salt, and soil. Sulfates form in the atmosphere from SO_2 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 anthropogenic 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.

The Great Smoky Mountains region frequently experiences poor visibility, and this is attributed to high emissions of biogenic aerosols from forest vegetation, anthropogenic aerosols from combustion sources, and high humidity (Ames et al. 2000, Day et al. 2000, Kim and Hopke 2006, Malm et al. 2000a, Malm et al. 2000b).

Human-caused visibility degradation at GRSM has largely been caused by atmospheric SO_4^{2-} due to anthropogenic SO_x emissions (Malm and Sisler 1987, Shaver et al. 1994). Emissions of NO_x may appreciably contribute to the problem on occasion. Organics are responsible for much of the remaining visibility impairment² (Malm and Sisler 1987). The contribution of SO_4^{2-} to the b_{ext} at the APHN is largest on the haziest days (Figure 2). On average, 71.5% of the total particulate light extinction was attributable to SO_4^{2-} , and that percentage increased to 79.0% on the 20% of the days that were haziest. On the clearest 20% of visibility days, the relative importance of SO_4^{2-} decreased to 58.2% and NO_3^- extinction became proportionately more important (12.1%) as compared with the haziest days when extinction attributed to NO_3^- was only 2.3% of the total light extinction.

Annual mean dv levels on the 20% 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 GRSM. Monitoring sites showing the largest differences during the period 2006-2008 between measured visibility on the clearest days and estimated natural conditions included SHEN, MACA, GRSM, and Washington, DC (NPS 2010). Kim and Hopke (2006) identified the major sources of $\text{PM}_{2.5}$ concentrations in the Great Smoky

² *Visibility impairment* means any humanly perceptible change in visibility (light extinction, visual range, contrast, coloration) from that which would have existed under natural conditions.

GRSM

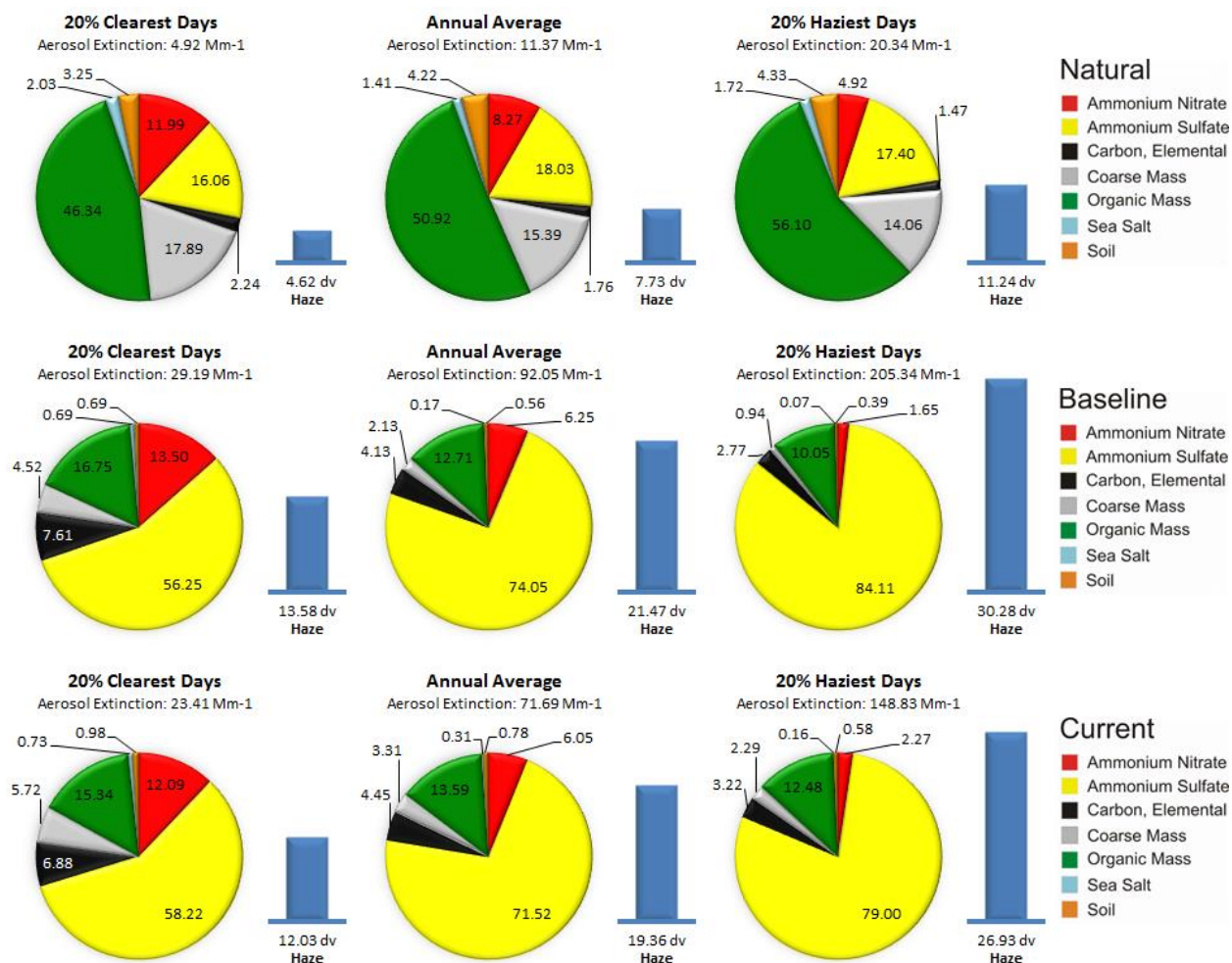


Figure 2. Estimated natural (pre-industrial), baseline (2000-2004), and current (2006-2010) levels of haze (blue columns) and its composition (pie charts) on the 20% clearest, annual average, and 20% hazeiest visibility days for GRSM. (Data Source: NPS-ARD)

Mountains, and their relative contributions to the PM_{2.5} total were estimated using a positive matrix factorization source apportionment approach (Paatero 1997). Three types of secondary SO₄²⁻ particles were identified as contributing heavily to PM_{2.5}, totaling 73% of the PM_{2.5}. Secondary NO₃⁻ particles contributed only 2% of the PM_{2.5} mass, some locally produced from transparticle NH₃. Gasoline vehicle emissions were tentatively separated from diesel emissions, accounting for 13% and 1%, respectively, of the total PM_{2.5}.

Research has been conducted in GRSM to characterize the effects of ambient aerosols on visibility in the park. The Southeastern Aerosol and Visibility Study (SEAVS) was conducted during the summer of 1995 (Hand et al. 2002). Measurements were made of aerosol light scattering coefficients, chemical composition, aerosol size distributions, hygroscopicity, and particle refractive index. Cheng and Tanner (2002) reported atmospheric measurements of fine (0.1-0.4 μm diameter) and ultrafine (< 0.1 μm diameter) particles and gaseous species in GRSM in 2000. A 6-factor model was constructed

which explained nearly 80% of the variation in the atmospheric data. More than one third of the variability was attributed to ultrafine particles. Levels of ultrafine particles are high in the atmosphere in the vicinity of GRSM. This is due to emissions of pollutants from anthropogenic and biogenic sources and abundant sunshine during summer (Cheng and Tanner 2002).

Trends in Visibility

Although ambient visibility in GRSM is substantially degraded, there is some indication that visibility conditions are improving in the park. Between 1996 and 2006, visibility in scenic areas improved on the 20% haziest days at five monitored locations throughout the United States, including GRSM (U.S. EPA 2008a). A small, but significant, improvement in visibility demonstrated at GRSM between 1990 and 2004 was largely due to a reduction in atmospheric SO_4^{2-} concentration. Model projections by VISTAS suggested that visibility at GRSM is likely to further improve substantially by 2018 under existing state and federal emissions regulations (U.S. EPA 2008a).

Available haze data collected at the GRSM IMPROVE site over the period of record are shown in Figure 3. Reductions in haze since 1990 have been most pronounced on the 20% haziest days, although some reductions in haze also have occurred on the 20% clearest and average days. However, this improvement may have slowed more recently. While an analysis of 2000-2009 data showed significant improvement in visibility on the clearest days, there was no improvement on the haziest days (NPS ARD 2013).

To date, progress towards compliance with the RHR at GRSM has been substantial (Figure 4). Nevertheless, continued progress in reducing haze levels on the haziest days will be needed.

Toxic Airborne Contaminants

Atmospheric deposition of toxic substances has not been well-studied in the APHN. Monitoring data indicate that GRSM receives relatively high levels of atmospheric Hg deposition. However, conditions in the park are not highly conducive to Hg methylation and the topic of Hg bioaccumulation has not been well-studied in this park or network.

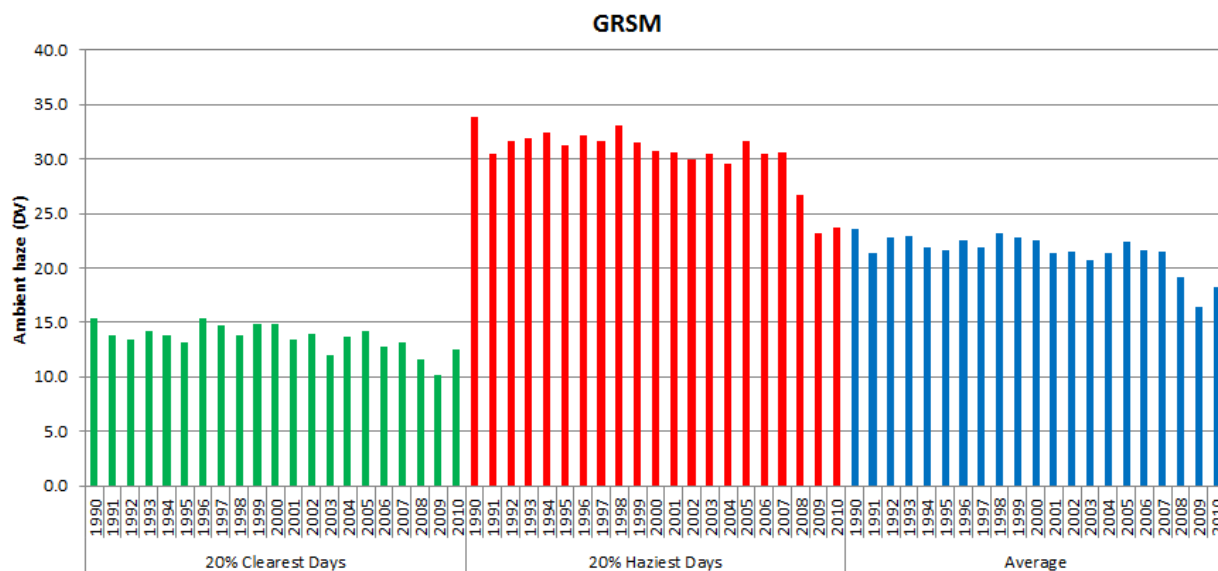


Figure 3 Trends in ambient haze levels at GRSM, based on IMPROVE measurements on the 20% clearest, 20% haziest, and annual average visibility days over the monitoring period of record. (Data Source: http://vista.cira.colostate.edu/improve/Data/IMPROVE/summary_data.htm)

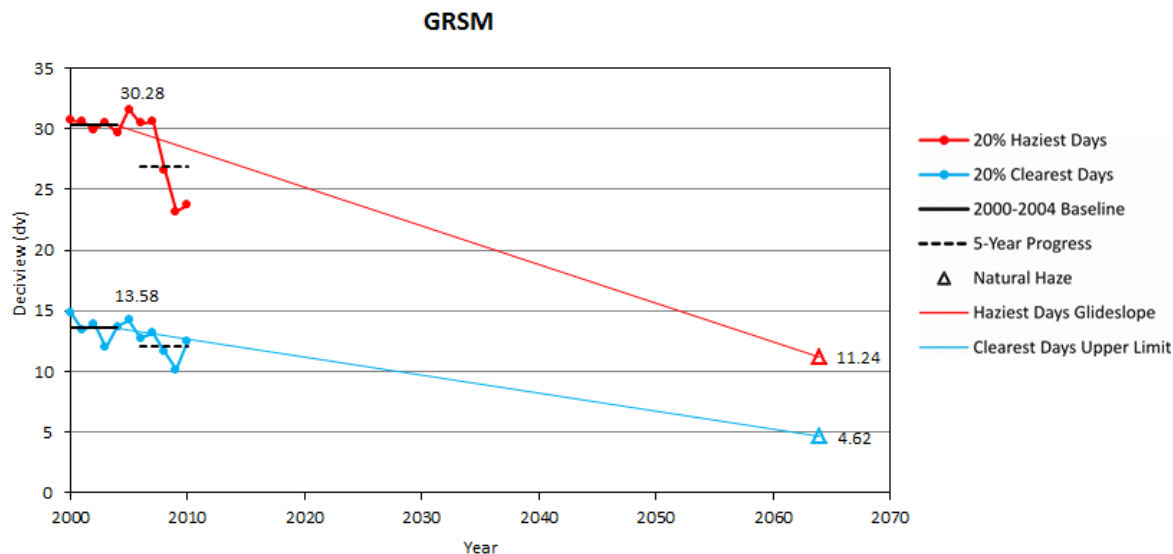


Figure 4. Glideslopes to achieving natural visibility conditions in 2064 for the 20% haziest (red line) and the 20% clearest (blue line) days in GRSM. In the regional haze rule, the clearest days do not have a uniform rate of progress glideslope; the rule only requires that the clearest days do not get any worse than the baseline period. Also shown are measured values during the period 2000 to 2010. (Data Source: http://vista.cira.colostate.edu/improve/Data/IMPROVE/summary_data.htm)

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