3. Acid Deposition Impacts on Aquatic and Terrestrial Ecosystems

Overview of Effects of Nitrogen and Sulfur Deposition:

The effects of deposition of nitrogen and sulfur compounds on natural systems include acidification of freshwaters (chronic and episodic), loss of aquatic species, eutrophication of estuarine and near-coastal waterways, soil nutrient and base cation leaching, and vegetation changes. Changes in water chemistry affect algae, fish, submerged vegetation, and amphibian and aquatic invertebrate communities. These changes can result in higher food chain impacts.

Scientific consensus is towards "(certainty) that human alterations of the nitrogen cycle have:
1) approximately doubled the rate of nitrogen input into the terrestrial nitrogen cycle, with rates still increasing,
2) increased concentrations of the potent greenhouse gas N_2O (nitrous oxide) globally,
3) caused losses of soil nutrients, such as calcium and potassium that are essential for long-term soil fertility,
4) contributed substantially to the acidification of soils, streams, and lakes in several regions
5) greatly increased the transfer of nitrogen through rivers to estuaries and coastal oceans,
6) increased the quantity of organic carbon stored within terrestrial ecosystems,
7) accelerated losses of biological diversity, especially losses of plants adapted to efficient use of nitrogen and losses of the animals and microorganisms that depend on them, and
8) caused changes in the composition and functioning of estuarine and nearshore ecosystems and contributed to long-term declines in coastal marine fisheries." (Vitousek, et al., 1997)

Nitrogen saturation conditions have been documented in a variety of ecosystem types in eastern and western North America. There are increasing reports of forests in the US that are nitrogen saturated, and reduction of nitrogen emissions is a preferable solution. (Fenn, et al. 1998)

Water data collected over the past 28 years in the northeastern U.S. indicate that while sulfate trends are declining in precipitation and in surface waters, stream acid neutralizing capacity (ANC) is not yet rebounding. (Clow, 1998). The lack of recovery in northeastern U.S. regions is attributable to strong regional declines in base-cation concentrations that exceed the decreases in sulfate concentrations (Stoddard et al., 1999)

Four National Park Service areas nationwide (Shenandoah National Park, Great Smoky Mountains National Park, Sequoia Kings Canyon National Parks, and Rocky Mountain National Park) and a Fish and Wildlife Service area in Florida (Chassohowitzka National Wildlife Refuge) have been the focus of extensive research on aquatic and/or terrestrial ecosystem impacts from nitrogen and sulfur deposition in the past two decades. The summaries below highlight the most recent peer-reviewed literature on deposition impacts to these four areas (and adjacent areas). The NPS has observed acidification of streams in both Shenandoah and Great Smoky Mountains NPs; scientists have documented nitrogen saturation in Rocky Mountain NP and episodic acidification in areas near the park. None of these areas are violating existing NAAQS for sulfur dioxide or nitrogen oxides. It is not clear whether all of these areas would also be in compliance with a new fine particle NAAQS because of uncertainty regarding method that will be used to determine compliance. There are likely other NPS and FWS areas around the country that are also experiencing deposition impacts, however insufficient information is currently available on the remainder of the parks and refuges.

Regional (Appalachian) Deposition Impacts Summaries:

Aquatic Ecosystems:
Extensive reviews of acidic deposition effects on Class I area aquatic resources have been conducted by the Southern Appalachian Mountains Initiative (SAMI). The August 1996 SAMI review report includes an annotated bibliography with summaries of relevant papers that provide new information since the 1990 NAPAP reports (Herlihy, 1996). Information provided in the SAMI report will not be reiterated in detail here, but general conclusions of the report will be presented, along with information from new papers published in 1996 and later.

The SAMI report considered it well-established that sulfate and nitrate from atmospheric deposition are the dominant source of acid anions in Southern Appalachian streams, that Class I areas in the Southern Appalachian area are much more sensitive to acidic deposition than the region as a whole, and that low pH and high aluminum are "causing damage to aquatic biota" (Herlihy, 1996).

Conceptual and predictive models have been increasingly used to predict deposition driven changes to aquatic ecosystems in the Appalachians. Predictive models such as NuCM and MAGIC have been calibrated with nitrogen and sulfur deposition field data with consistent results, and ecosystem field data from the central Appalachian region has documented seven symptoms of nitrogen saturation and confirmed nitrogen saturation conceptual models (Peterjohn, 1996).

Terrestrial Ecosystems:
SAMI has also developed an overview of acidic deposition effects on terrestrial ecosystems (primarily high-elevation spruce-fir forests) in southern Appalachian Class I areas (Eagar, 1996). Again, the highlights of the SAMI terrestrial report will be briefly touched on here, but the focus of the discussion below will be to emphasize new information published in 1996 or later.

Aluminum released to water in the mineral soil by acid rain decreases the availability of calcium in the northeast red spruce forest floor, the primary layer for nutrient uptake by roots in forest soils (Lawrence, 1995). Regional assessments of forest soil chemistry (including Shenandoah NP sites) supports evidence of soil-calcium depletion in the northeast; acid rain is identified as a probable factor (Lawrence, 1997) Dendrochemical and biochemical markers (Al and Ca) link stress in otherwise healthy red spruce trees in the northeast US to acidic deposition. (Shortle, et al. 1997)

Cloud water may add ecologically significant amounts of pollutants and nutrients to many ecosystems in the northeastern U.S. Cloud water is a significant source (30% -38%) of nitrogen and sulfur at Great Smoky Mountains NP (Li & Aneja, 1992; Cole, 1992). At least 11 peer-reviewed studies documented high acidity in cloud water chemistry in the eastern U.S. (Li & Aneja, 1992). 90% of clouds sampled over a three year period in Great Smoky Mountains NP were acidic (pH <5.0). Concentrations of sulfate and nitrate in cloudwater at four eastern sites (including Shenandoah NP) were found to be 7-43 times as high as in rainwater. (Weathers et al. 1986). Chamber experiments on red spruce seedlings and field measurements on red spruce trees at Whitetop Mountain in Virginia found that cloudwater exposure is likely affecting the health of red spruce trees by decreasing foliar Ca, Mg, and Zn levels in trees such that tree growth is affected, and by decreasing cold tolerance of seedlings such that they are more susceptible to winter injury. (Thornton et al. 1994)

Shenandoah NP Deposition Impacts Summaries:

Shenandoah NP Aquatic Ecosystem Impacts:

Episodic acidification (ANC loss) is "ubiquitous" in Shenandoah NP streams, and is primarily caused by temporal increases in sulfate, nitrate, and organic acids (Hyer, 1995). During storm events, pH and ANC decrease (ANC falls below zero in Paine Run, a particularly sensitive stream), and sulfate and nitrate concentrations increase. Analysis of three years of data for three Shenandoah watersheds indicates that precipitation input of sulfur and nitrogen is of dominant importance as a principle driver to the episodic acidification response of the study watersheds. In addition, atmospheric sulfate deposition has been more closely linked with episodic streamwater changes than has nitrate deposition. (Eshelman et al., 1999).

Chronic acidification of surface water is also a serious concern in Shenandoah NP. In the White Oak Run watershed in Shenandoah, sulfate concentrations in streamwater have been increasing over the last 10-20 years (Herlihy, 1996). Sulfate is the major anion in most streams with low ANC, and catchments are retaining a significant proportion of atmospherically deposited sulfur (Cosby et al., 1991). Values of pH as low as 5.0 are common in Shenandoah streams (Bulger et al. 2000a).

In addition to anthropogenic deposition contributions of nitrate in Shenandoah's aquatic and terrestrial ecosystems, forest defoliation by gypsy moth caterpillars in 1990 has also influenced nitrate additions to Shenandoah watersheds. This event has increased stream chemistry nitrate in the last decade in Shenandoah NP, by reducing the amount of N uptake usually provided by the trees or by otherwise altering biogeochemical processes that contribute to nitrogen retention, and thus causing episodic and chronic leakage of nitrate from the watershed (Eshleman, et al. 1995 and Webb, et al. 1995). The forest defoliation has also accelerated the export of base cations from the watershed, which in the short-term neutralizes some of the nitric acidity, but may over a longer period limit the recovery of the watershed from the effects of chronic atmospheric acidic deposition (Eshelman et al., 1998)

Several initial indicators of fish community, population, and organism level decline related to chronic and episodic stream acidification have been documented in Shenandoah NP. These include:

- Black-nosed dace fish have reduced growth in low ANC streams compared to higher ANC streams, possibly because in low ANC streams they must spend energy on ion regulation rather than growth (Dennis, 1995a and Dennis, 1995b)
- Fish survivorship declined from 80% to 0% at Paine Run (a low ANC stream in Shenandoah NP) coincident with a sharp drop in pH (and peaks in toxic aluminum concentrations) during

large storm water inputs in 1993 that produced “acute acidification” in that stream (Bulger, 2000a.)

- Trout embryo survivorship is significantly affected by water chemistry in Shenandoah NP: survivorship was lower in poorly buffered streams, and episodic acid pulses were associated with trout embryo mortality. (MacAvoy and Bulger, 1995)
- Trout populations (production and density) are smaller in poorly buffered (low ANC) streams than in well buffered streams in Shenandoah NP (Newman and Doloff, 1995)
- Fish species richness in some sensitive Shenandoah streams may have been lowered by acidification. Although direct linkages between deposition impacts and loss of fish species from streams has not yet been proven, it has been shown that streams with low ANC host fewer species of fish (80% of the variance in fish species number in a sample of 11 Shenandoah NP streams can be explained by minimum ANC) (Bulger et al., 1995).
- The black-nosed dace population in Meadow Run (the lowest ANC stream studied in Shenandoah NP) declined since fish populations were first studied there, and this species is now considered extirpated from that stream. (Bulger, 2000a)

Native brook trout viability potential has been established in Virginia for 60 streams (representing the population of 300 brook trout streams in Virginia that are at risk from acidic deposition). This sample includes 14 streams in Shenandoah NP. These streams were categorized as either: “non acidic” (ANC above 50 ueq/l both episodically and chronically), “indeterminate” (ANC 20-50 ueq/l chronically with possible episodic acidification events), “episodically acidic” (ANC 0-20 ueq/l average), or “chronically acidic” (ANC < 0). The study indicated that approximately 30% of all trout streams in Virginia are either “chronically (6%) or episodically (24%) acidic and therefore either marginal or unsuitable for brook trout (Bulger, et al. 2000b). In addition, model simulation shows that 82% of the contribution to stream acidification is anthropogenic. Model simulations (using the aquatic ecosystems effects model MAGIC) project that greater than 70% reduction in sulfate deposition would be needed to change stream chemistry such that the number of streams suitable for brook trout viability would increase (Figure 1). 70% reduction in deposition (from 1991 levels) is needed to simply prevent further increase in Virginia stream acidification. (Bulger, et al., 2000b)

NuCM modeling was conducted as a part of SAMI (Southern Appalachian Mountains Initiative) for White Oak Run and Shaver Hollow watersheds in Shenandoah NP. White Oak Run appears to be the more deposition-sensitive watershed. For White Oak Run, sulfate concentrations in streams are expected to increase even with no increases in atmospheric sulfate inputs. These increases in sulfate concentration would decrease alkalinity from current levels of 15 ueq/l, to –5 ueq/l. NuCM modeling agrees with the MAGIC modeling (above), also indicating that it would take 70% reductions in sulfate deposition to maintain watershed sulfate at current levels. Because these systems appear to be sulfate dominated, changes in nitrate deposition affect stream nitrate concentrations only slightly. All modeling scenarios show declines in Ca/Al ratios suggesting that forest stress is likely to increase over time (Munson, 1998).

Sulfur deposition background rates (from the late 1800s) are considered to be around 4 kg/ha/yr (Herlihy, 1996). Overall, total nitrogen deposition (wet and dry) in the park is about 9.5 kg/ha/yr for nitrogen (38% contribution from dry and 62% from wet) and around 8 kg/ha/yr sulfur (36% contribution from dry and 64% from wet) (Figures 2 and 3). The contribution to total nitrogen and sulfur deposition from cloud water in Shenandoah is uncertain, but an attempt should be made to estimate it for any forecasting models that assess impacts of total deposition.

Shenandoah NP Conclusions:
Research studies indicate that chronic and episodic acidification have affected fish in Shenandoah's sensitive aquatic ecosystems at the community level (reduced species richness in streams), population level (mortality of brook trout), and organism level (reduced growth in black nosed dace). This is a serious situation that merits immediate action to reduce deposition impacting Shenandoah fish species. Two separate ecosystem effects models produced similar results indicating that sulfate deposition reductions greater than 70% are needed to prevent additional stream alkalinity reductions and brook trout stream losses in Virginia.

Great Smoky Mountains NP Deposition Impacts Summaries:

Great Smoky Mountains NP Terrestrial Ecosystems Impacts:
Great Smoky Mountains National Park contains 74% of the spruce-fir forests in the Southern Appalachians, making the park the largest remnant red spruce-Fraser fir ecosystem in the world. Recent studies indicate that spruce-fir forests in Great Smoky Mountains NP are undergoing greater stress than spruce-fir in other parts of the region (Eager, 1996). One significant contributor to that stress may be atmospheric deposition inputs to forest soil-water chemistry.

Nitrogen saturation in eastern forest ecosystems occurs when atmospheric sources (N deposition) and biological sources (N mineralization) of nitrogen exceed the N uptake capacity by biotic organisms. Nitrogen saturation is induced when increased rates of N deposition cause increased leaching (export) of nitrate, which in turn causes soil and water acidification. Losses of base cations (Ca and Mg) from soils and the mobilization of soil Al, then contribute to nutritional imbalances and growth decreases in trees along with water quality degradation (Garten and Van Miegroet, 1994). Modeling runs (with the NuCM model) show that S and N deposition are the major factors affecting soil solution chemistry in red spruce forests in Great Smoky Mountains. A 50% modeled reduction in N and S deposition caused a rapid reduction in NO_3 and SO_4 and Al concentrations in soils within the first three years of modeling runs. (Johnson, et al., 1999).

Great Smoky Mountains NP Aquatic Ecosystems Impacts:
Great Smoky Mountains NP streams contain the southern-most range of endemic brook trout populations in the country. These streams are very sensitive to acidic deposition and many high elevation streams are currently acidic (ANC ranged from -31 ueq/l to 28 ueq/l in five sensitive Great Smoky Mountains streams over a two year period). (Cook, 1994). Great Smoky Mountains stream surveys in 1993 and 1994 observed high nitrate levels in both spring and fall, suggesting that many systems are reaching an "advanced stage of nitrogen saturation" (Flum, 1995; and Stoddard, 1994). In addition, sulfur isotope analysis indicates that most of the sulfate in stream water in the five study areas in Great Smoky Mountains likely comes from atmospheric deposition (Cook, 1994). Dry deposition monitoring data is not yet available for Great Smoky Mountains, however yearly average wet deposition and concentration (Figure 4) represent some of the highest sulfate deposition loading in the country (Figure 5). In addition, trend analysis suggests that wet nitrate deposition at the Great Smoky Mountain NADP site has increase by approximately 20% over the past 18 years (Figure 6).

Great Smoky Mountains streams in the high elevation Noland Divide watershed are particularly vulnerable. Monitored over a 8 year period, ANC was consistently < 20 ueq/l, pH was consistently <6, nitrate ranged from 35-70 ueq/l, and sulfate ranged from 20-50 ueq/l. Noland Divide watershed is "Stage 2 nitrogen saturated" (nitrogen export is very high, on the order of 21 kg N /ha/yr): contributing to both chronic and episodic streamwater acidification and export of calcium (Nodvin, 1995; Cole, 1992). A "storm event study" was conducted at Noland Divide from October 31 to November 5, 1995, to document the effects of episodic acidification on streamwaters. During the storm event, the pH decreased by a whole pH unit to 4.9 and nitrate and sulfate increased by 24-33 ueq/l (Smoot, et al., 2000). These episodic changes in stream chemistry may have a greater impact on aquatic biota than chronic stream chemistry changes.

Extensive long-term streamwater sampling in Great Smoky Mountains NP has shown that streamwater nitrate concentrations, are strongly correlated with elevation, (Figure 7) as are sulfate, pH and ANC (Smoot et al., 2000). Nitrate, and sulfate concentrations increase with elevation, and pH and ANC decrease with elevation. Nine of ninety streams sampled over an eight year period in Great Smoky Mountain NP had median pH values less than or equal to 5.6, the lower limit for brook trout population viability. Time trend analysis showed a statistically significant decreasing trend in pH over the eight year study period, at all elevation classes (Smoot, et al., 2000).

NuCM modeling conducted as a part of SAMI for Noland Divide in Great Smoky Mountains projected that streamwater concentrations of sulfate would decrease by about 22% if sulfate deposition was reduced around 70%. Forest stress reductions (changes in Ca/Al ratios) were also projected in response to 50% and 70 % reductions in sulfur deposition. Streamwater nitrate was more responsive to changes in nitrate deposition, and was projected to decrease about 50% if nitrate deposition were to drop by 40%. (Munson, 1998)

MAGIC modeling also conducted for SAMI for the same watersheds showed similar results to the NuCM modeling runs. Model simulations indicate that reductions of sulfate deposition of 50%-70% would be necessary to prevent further increases in annual average stream sulfate concentrations at Noland Divide. Streamwater nitrate modeling results showed that streamwater response to changes in nitrate deposition are relatively rapid and that stream water nitrate concentration changes are proportional to nitrate deposition changes. Overall, model runs for stream alkalinity indicated that reductions in total acidity of deposition of at least 55% are necessary to prevent annual average stream alkalinity from becoming negative (Cosby, 1998).

Great Smoky Mountain NP Conclusions:
Great Smoky Mountains NP streams are experiencing chronic and episodic acidification that is caused, in a large part, by acidic deposition. Noland Divide watershed, is currently at "stage 2" nitrogen saturation, exporting large amounts of nitrogen into park streams during the growing season. Stream pH is declining at all elevations in the park. Acidic deposition is also causing forest ecosystems to experience chemical imbalances that are contributing to tree stress. Two separate types of ecosystem models concur that sulfate and nitrate deposition reductions of 70% and 40% respectively are necessary to prevent acidification impacts from increasing in Great

Smoky Mountains ecosystems. Deposition reductions above and beyond these amounts are necessary to improve currently degraded aquatic and terrestrial ecosystems.

Cloud water deposition impacts need to be considered by EPA when assessing emissions reductions needed to achieve future critical load recommendations. If cloud water contributes a significant portion of the nitrogen and sulfur impacting terrestrial ecosystems in Great Smoky Mountains, and cloud water is not currently measured in deposition monitoring networks, total deposition loading currently impacting park ecosystems may need to be substantially revised upward.

<u>Rocky Mountain National Park Deposition Impacts Summaries:</u>

Rocky Mountain NP Aquatic Ecosystems Impacts:

At Rocky Mountain NP and other high elevation watersheds in the Colorado Front Range, researchers have documented that there has been a shift in ecosystem dynamics over the past few decades from an N-limited system to an N-saturated system as a result of anthropogenic N in wetfall and dryfall (Williams et al., 1996). Source attribution of nitrogen contributions to the Colorado Front Range has not been done extensively, however, it is clear that while high elevation ecosystems in the Colorado Rockies are influenced by air pollution sources located on both sides of the Continental Divide, sources of nitrogen and sulfur located east of the Divide have a greater influence on precipitation chemistry in the Colorado Rockies than those on the west side (Heuer et al., 2000).

Annual deposition of inorganic N in wetfall at Niwot Ridge, (a University of Colorado Research Station approximately 30 km from Rocky Mountain NP and at similar elevation) almost doubled from 1.95 kg/ha/yr for the 4-yr period from 1985-1988 to 3.75 kg/ha/yr for the 4 yr period from 1989-1992. Concurrent increases in $N0_3$ concentration of surface waters during snowmelt at this site are consistent with “Stage 1” of nitrogen saturation. In addition, the data show a trend of increasing values of $N0_3$ in surface waters during the growing season, which is consistent with initiation of “Stage 2” nitrogen saturation (Williams and Tonnessen, 2000). ANC has been concurrently decreasing at one of the Niwot Ridge lakes (Green Lakes 4) since the mid 1980s. Measurements of dry nitrogen deposition in 1993 and 1994 at Niwot Ridge ranged from 2.5-3.1 kg/ha/yr (Sievering, et al. 1996). Total dry deposition is commonly estimated at Niwot Ridge in the range of 25-50% of total deposition (which indicates that total deposition is around 5-7.5 kg/ha/yr).

Elevated nitrate concentrations reported at a Niwot Ridge study lake, also occur throughout wilderness areas in the Colorado Front Range, but not in wilderness areas to the west of the Colorado Front Range. $N0_3$ concentrations at high elevation lakes on the eastern slope of Colorado’s Front Range were significantly greater (a range of 6.3 to 8.1 umol/l) than on the western slope (1.9 umol/l) (Williams and Tonnessen, 2000) (Figure 8).

Loch Vale watershed, a long-term study area in Rocky Mountain NP, west of the metro-Denver area receives yearly N deposition in the range of 3-5 kg/ha/yr. Approximately 36% of the nitrogen deposition at this site comes in dry form and 64% in rain and snow (Figure 2). These deposition levels are greater than those considered background (0.2kg/ha/yr typical of remote, non-industrialized parts of the world. (Baron and Campbell, 1997) and can also be compared to sites on the western slope of the continental divide which receive 1-2 kg/ha/yr total deposition (Baron et al., 2000). No trend has been detected in NO_3 increases at Loch Vale over the period that wet deposition has been monitored at the site, however, NH_4 concentrations have been increasing significantly.

A cumulative assessment of multiple studies over the past two decades in Rocky Mountain NP indicate that increased emissions from stationary, mobile, and agricultural sources on the east side of the Colorado Front Range can be linked (via comparisons between east and west side terrestrial and aquatic plots, deposition gradients, and nitrogen isotopic ratios) to increased nitrate or nitrogen in soils, streams, lakes, and spruce trees in Rocky Mountain NP, as well as to changes in lake diatom community composition over time (Baron et al., 2000). This finding provides a large body of concurrent and corraborative studies that point to extensive, although subtle to detect, terrestrial and aquatic ecosystem deposition impacts currently occurring at Rocky Mountain NP.

Nitrogen deposition inputs at Lock Vale are currently greater than nitrogen used by ecosystem processes and biota; therefore, Loch Vale is considered nitrogen saturated. Nitrogen budgets developed from research study results in the Loch Vale watershed in Rocky Mountain NP indicate that of the 3.9 kg/ha/yr average of N deposition (wet and dry) received by the watershed, 49% of the N was immobilized and 51% of the N (2.0kg/ha/yr) left the ecosystem via the stream. Alpine tundra used 18% of the N inputs to the ecosystem, 5% was incorporated into forest vegetation and soils, aquatic algal uptake accounted for 15% of the total inputs, and biological activity within talus accounted for 11%. (Baron and Campbell, 1997) . Therefore it may be reasonable to conclude that about a 50% reduction in N deposition would be needed before the N deposited is in balance with the N used by the ecosystem, and nitrogen saturation at that site would be reversed.

Rocky Mountains NP Terrestrial Ecosystems Impacts:

While current deposition rates in the Colorado Front Range are low compared to those found in the eastern U.S., they are high in the context of internal N cycling (low N mineralization rates and low biotic uptake) in these alpine ecosystems. Therefore the potential for impacts of anthropogenic N deposition in Colorado alpine ecosystems is relatively high (Bowman, 2000). Alpine community productivity and species diversity are constrained by the supply of N. Field studies of alpine plants indicate that increases in N availability (above current levels) may lead to changes in alpine plant species composition (replacement of meadow forbs such as *Acomastylis rossii* by meadow grasses such as *Deschampsia caespitosa*) as a result of competitive displacement in the Colorado Front Range (Bowman and Stelzer, 1998). This shift mirrors changes found in nitrogen impacted areas in Europe toward grassland dominated communities. Changes in these species have implications for altered N cycling in soils and plants and shifts in species are likely to result in increased N flux from terrestrial into aquatic ecosystems (Bowman and Stelzer, 1998).

Soils in forest plots on the east and west sides of the Colorado Front Range had similar characteristics except that soils had significantly higher nitrogen percentages on the east side than on the western slope. Microbial N mineralization rates were also significantly higher in the east side plots, and this additional source of N will contribute to the available NO3, in the soils, exacerbating N saturation (Baron et al, 2000). Higher N:P ratios in Bristlecone Pines (*Pinus aristata*) (Williams et al., 1996) and lower C:N ratios (Baron et al., 2000) have been documented in forested ecosystems of the Colorado Front Range. These changes in foliage chemistry can be related to higher additions of N deposition along an elevational and depositional gradient, raising concerns about the ability of these species to resist winter foliage damage. (Williams and Tonnessen, 2000)

Rocky Mountain NP Conclusions:
Cumulative evidence from multiple studies in Rocky Mountain NP and adjacent areas along the Colorado Front Range strongly suggests that current levels of wet nitrogen deposition (3-5kg/ha/yr) are altering terrestrial and aquatic ecosystems on the eastern slope of the mountains.

Williams and Tonnessen (2000),assert that there is currently sufficient science to support setting critical loads (of wetfall) for the Colorado Front Range at 4kg/ha/yr . Baron et al.(2000) suggests that critical loads should be set somewhere between 3-5 kg/ha/yr. Scientists suggest that land managers may wish to set target loads at a lower level to allow a margin of safety to protect very sensitive resources (Williams and Tonnessen, 2000). Nitrogen budget research appears to indicate that approximately 50% reduction in total nitrogen deposition could be needed to reverse nitrogen saturation in Rocky Mountain NP aquatic and terrestrial ecosystems.

Sequoia National Park Deposition Impacts Summaries:

General Sierra Nevada Aquatic Ecosystem Impacts:
A 5-year study of seven watersheds in the Sierra Nevada showed that in most lakes, ANC depression is the result of lake water dilution by snowmelt. There were however, lakes where acidification (increasing anion concentration) was noted. In these lakes, nitrate and sulfate were equally important contributors to acidity during the first half of snowmelt, while sulfate dominated the latter half. (Leydecker et al., 1999)

Watershed modeling estimates that in the Sierra Nevada Range, presently up to 1.8% of the Sierra Nevada lakes may undergo snowmelt ANC depressions slightly below zero. The model also predicted that if acidic deposition increased by 50% increase, approximately 6% of Sierra Nevada lakes would become episodically acidic. (Leydecker et al., 1999)

Sequoia NP Aquatic Ecosystem Impacts:
At the Emerald Lake long-term study watershed in Sequoia NP, two documented episodic acidification events in the 1983-1993 time period showed NO_3 concentration of surface waters sufficient to drive ANC to zero. Other studies at Emerald Lake indicated that transformations of NH_4 within the basin appear to be one cause of episodic acidification of surface waters. Episodic acidification driven by N dynamics has apparently resulted in increased leaching of base cations from the basin in excess of cation production from geochemical weathering (Williams, et al., 1995). The situation at Emerald Lake may be improving, however: a decrease in NO_3 concentrations over the past decade represents a shift from Stage 2 nitrogen saturation (chronic N export during the growing season) to Stage 1 nitrogen saturation (chronic N export during the

non-growing season) (Sickman and Melack, 1998). SO_4 concentration in Emerald lake in Sequoia NP was found to increase with increasing stream discharge, suggesting that atmospherically deposited SO_4 is temporarily stored and its release is controlled by the extent of soil water flushing (Williams and Melack, 1997). Watershed modeling (Alpine Hydrochemical Model) demonstrated that Emerald Lake is particularly sensitive to high runoff rates and acidic loadings in precipitation (Wolford and Bales, 1996).

A few other lakes in Sequoia NP have been studied to assess nitrogen deposition impacts. Topaz Lake in Sequoia NP has been characterized as falling somewhere between Stage 1 and Stage 2 of N saturation, however, scientists note that what is commonly considered Stage 1 N saturation in other parts of the country is considered by some scientists to be a natural condition representing NO_3 derived from catchment sources. (Sickman and Melack, 1998)

Field experiments have been conducted on stream aquatic biota (macroinvertebrates) to assess atmospheric deposition impacts in Sequoia NP (Kratz, 1994). Artificial pH pulses of pH 5.2 and pH 4.6 showed that several species are potentially sensitive (reduced densities) to pH reductions in the park should they occur in the future.

Total deposition of nitrogen (wet and dry) at Sequoia NP is in the 5-6 kg/ha/yr range. About 50% of the nitrogen deposition falls as rain and snow and 50% falls as dry deposition (Figure 3).

Sequoia NP Conclusions:
Acid rain and snow is not as much of a problem to high-elevation aquatic and terrestrial ecosystems in the Sierra Nevada Range as in the eastern U.S. or in the Colorado Rockies. Chronic acidification has not been demonstrated, however, episodic acid pulses can occur during spring snowmelt causing lake ANC to fall below 0 ueq/l. (Stoddard, 1995). Emerald Lake, the principal long-term study lake in Sequoia NP, has not experienced long-term pH or ANC changes due to acidic deposition , based on examination of diatom cores (Holmes et al., 1989), however, episodic acidification events have been documented at the lake. It is unknown what specific impacts these acid pulses may have on aquatic biota, but based on results of some field experiments, it is possible that some macroinvertebrate species may be impacted during these events.

Emerald lake and many other high elevation lakes in Sequoia are extremely sensitive (have low buffering capacity) to any future acidic deposition inputs, and it is therefore important that additional deposition loadings to the park are minimized.

Nitrogen Effects to Coastal National Wildlife Refuges:

The FWS is conducting a multi-year study (1996-present) to evaluate the potential for adverse environmental effects from atmospheric nitrogen in Chassahowitzka National Wildlife Refuge (Dixon and Estevez, 1999). Phytoplankton, submerged aquatic vegetation, and water chemistry have been sampled quarterly. The trophic status of the area and indicators of eutrophication have also been assessed quarterly.

Water quality and trophic status were rated as good in 1996 and 1997. Inorganic nitrogen to inorganic phosphorous ratios indicated that the system was nitrogen-limited. In 1998, a phytoplankton bloom developed and persisted for months, degrading water quality and causing trophic status to fall into the poor range. The bloom was caused by excess nitrogen in offshore waters following an unusual discharge event from a nearby watershed river. It is not known what portion of the nitrogen was atmospheric in origin (from direct deposition to the offshore waters and deposition to the watershed) versus terrestrial run-off.

Coastal National Wildlife Refuge Conclusions:

The phytoplankton bloom is evidence that the system is sensitive to nitrogen inputs and is already experiencing, at times, nitrogen in excess of the ecosystem's needs. If nitrogen inputs continue at their present level, the system may experience additional phytoplankton blooms, with loss of water quality and other symptoms of eutrophication, including loss of submerged aquatic vegetation, essential to coastal fish and wildlife.

FWS manages many other coastal areas that may already be experiencing eutrophication due to excess nitrogen, including Brigantine Wilderness (New Jersey) and Swanquarter Wilderness (North Carolina).

National Trends in Nitrogen and Sulfur Deposition Conclusions:

The NPS has been examining trends for a variety of air quality-related parameters to assess progress in meeting performance goals developed in response to the Government Performance and Results Act. The NPS trend analysis for acid deposition looks at sulfate and nitrate ion concentrations in wet deposition, using a 10-year rolling average and a significance value of p = .15. These analyses show that sulfate ion concentration trends in NPS units across the country (Figure 9) are generally consistent with national trends at urban and other sites that show sulfate ion concentration (in wet deposition) decreasing. The exceptions are some park units in the South that are not seeing decreases in sulfate ion concentrations (Guadalupe Mountains, Big Bend, Oregon Pipe Cactus, and Everglades National Parks). However, despite declining sulfate trends, the present rate and extent of expected sulfate emissions reductions will likely not be sufficient to reverse ecosystem degradation attributable to atmospheric acidic inputs.

The NPS trend analysis also documents that there are many park units where nitrate ion concentration is increasing (Figure 10). In addition, NADP maps make it clear that nitrate deposition in the past 15 years has been increasing in the southeastern U.S. (Figure 11) and that nitrate concentrations in some parts of the western U.S.(like Rocky Mountain National Park) are approaching nitrate concentrations as high as those commonly found in the northeastern U.S. (Figure 12). In addition, increases in ammonium over the last 15 years are likely exacerbating nitrogen saturation problems in park areas where nitrogen deposition impacts are currently a concern (Figure 13).

Modeling (with MAGIC, NuCM or other ecosystem impacts models) has been useful in predicting the amount of emissions reductions needed to halt or reverse ecosystem impacts in parks. These models can be applied to establish the amount of emissions reductions needed to protect aquatic and terrestrial resources in parks and wildlife refuges.

References

Baron J.S., H.M. Rueth, A.M. Wolfe, K.R. Nydick, E.J. Alstott, J.T. Minear, and B. Moraska. 2000. Ecosystem responses to nitrogen deposition in the Colorado Front Range. *Ecosystems* 3:352-368.

Baron J.S., and D.H. Campbell. 1997. Nitrogen fluxes in a high elevation Colorado Rocky Mountain Basin. *Hydrological Processes* 11:783-799

Bowman W.D., and H. Steltzer. 1998. Positive feedbacks to anthropogenic nitrogen deposition in Rocky Mountain alpine tundra. *Ambio* 27(7).

Bowman W.D. 2000. Biotic controls over ecosystem response to environmental change in alpine tundra of the Rocky Mountains. *Ambio* 29(7).

Bulger, A.J., C.A. Dolloff, B.J. Cosby, K.N. Eshleman, J.R. Webb, and J.N. Galloway. 1995. The "Shenandoah National Park: Fish in sensitive habitats" (SNP: Fish) project. An integrated assessment of fish community responses to stream acidification. *Water Air and Soil Pollution* 85: 309-314.

Bulger, A.J., B.J. Cosby, C.A. Dolloff, K.N. Eshleman, J.R. Webb, and J.N. Galloway. 2000(a). *Shenandoah National Park: Fish in Sensitive Habitats Final Report*. University of Virginia and Virginia Polytechnic Institute and State University. Report to the National Park Service, Coop Agreement CA-4000-2-1007.

Bulger, A.J., B.J. Cosby, and J.R. Webb. 2000(b). Current, reconstructed past, and projected future status of brook trout (salvelinus fontinalis) streams in Virginia. *Canadian Journal of Fish and Aquatic. Sci* 57: 1515-1523.

Clow, D.W., and M.A. Mast. 1998. Long-term trends in stream water and precipitation chemistry at five headwater basins in the northeastern United States. *Water Resources Research* 35(2):541-554.

Cole, D.W. 1992. Nitrogen Chemistry, Deposition, and Cycling in Forests. *In Atmospheric Deposition and Forest Nutrient Cycling*. D.W. Johnson and S.E. Lindberg, editors. Ecological Studies, 91. Springer-Verlag.

Cook, R.B., J.W. Elwood, R.R. Turner, M.A. Bogle, P.J. Mulholland, and A.V. Palumbo. 1994. Acid-base chemistry of high-elevation streams in the Great Smoky Mountains. *Water, Air and Soil Pollution* 72:331-356.

Cosby, B.J., P.F. Ryan, J.R. Webb, G.M. Hornberger, and J.N. Galloway. 1991. Mountains of West Virginia. *In Acid Deposition and Aquatic Ecosystems: Regional Case Studies.* D.F. Charles, editor. Springer-Verlag. NewYork.

Cosby, B.J., and T.J. Sullivan. 1998. *Final Report: Application of the MAGIC model to selected catchments: Phase I, Southern Appalachian Mountains Initiative (SAMI).* Department of Environmental Sciences, University of Virginia, Charlottesville, VA. September 1, 1998.

Dennis, T.E., S.E. MacAvoy, M.B. Steg, and A.J. Bulger. 1995(a). The association of water chemistry variables and fish condition in streams of Shenandoah National Park, USA. *Water, Air and Soil Pollution* 85: 365-370.

Dennis, T.E., and A.J. Bulger. 1995(b). Condition factor and whole-body sodium concentrations in a freshwater fish: evidence for acidification stress and possible ion regulatory over-compensation. *Water, Air and Soil Pollution* 85: 377-382.

Dixon, L.K., and E.D. Estevez. 1999. *Reservoirs of Nitrogen and Phosphorous Across a Multiple-source, Nitrogen-enriched, Estuarine Gradient.* Draft. Mote Marine Laboratory. Sarasota, Florida.

Eagar C., H. Van Miegroet, S.B. McLaughlin, and N.S. Hicholas. 1996. *Evaluation of Effects of Acidic Deposition to Terrestrial Ecosystems in Class I Areas of the Southern Appalachians*. A report to the Southern Appalachian Mountains Initiative (SAMI).

Eshelman, K.N., J.L. Moody, K.E. Hyer, and F.A. Deviney. 1999. *Episodic Acidification of Streams in Shenandoah National Park, Virginia.* Final Report from Cooperative Agreement #4000-2-1007 (Supplement #4) to: Department of Interior, NPS- Mid-Atlantic Region (University Park, PA) and NPS – Air Resouces Division (Denver, CO). December 31, 1999.

Eshelman, K.N., R.P. Morgan II, J.R. Webb, F.A. Deviney, and J.N. Galloway. 1998. Temporal patterns of nitrogen leakage from mid-Appalachian forested watersheds: Role of insect defoliation. *Water Resources Research* 34(8):2005-2116.

Eshleman, K.N., L.M. Miller-Marshall, and J.R. Webb. 1995. Long-term changes in episodic acidification of streams in Shenandoah National Park, Virginia (USA). *Water, Air and Soil Pollution* 85: 517-522.

Fenn, M.E., M.A. Poth, J.D. Aber, J.S. Baron, B.T. Bormann, D.W. Johnson, A.D. Lemly, S.G. McNulty, D.F. Ryan, and R. Stottlemyer. 1998. Nitrogen excess in North American ecosystems: a review of predisposing factors, geographic extent, ecosystems responses, and management strategies. *Ecological Applications* 8:706-733.

Flum, T., and S.C. Nodvin. 1995. Factors affecting streamwater chemistry in the Great Smoky Mountains, USA. *Water, Air and Soil Pollution* 85: 1707-1712.

Garten, C.T., and H.V. Miegroet. 1994. Relationships between soil nitrogen dynamics and natural N15 abundance in plant foliage from Great Smoky Mountains National Park. *Canadian Journal of Forest Research* 24.

Herlihy, A.T., P.R. Kaufmann, J.L. Stoddard, K.N. Eshleman, and A.J. Bulger. 1996. *Effects of Acidic Deposition on Aquatic Resources in the Southern Appalachians with a Special Focus on Class I Wilderness Areas*. Prepared for the Southern Appalachian Mountains Initiative (SAMI).

Heuer, K., K.A. Tonnessen, and G.P. Ingersoll. 1999. Comparison of precipitation chemistry in the Central Rocky Mountains, Colorado, USA. *Atmospheric Environment* 34 (2000) 1713-1722.

Holmes, R.W., M.C. Whiting, and J.L. Stoddard. 1989. Changes in diatom-inferred pH and acid neutralizing capacity in a dilute, high elevation Sierra Nevada lake since A.D. 1825. *Freshwater Biology* 21, 295-310.

Hyer, K.E., J.R. Webb, and K.N. Eshleman. 1995. Episodic acidification of three streams in Shenandoah National Park, Virginia, USA. *Water, Air and Soil Pollution* 85: 523-528.

Johnson, D.W., R.B. Susfalk, P.F. Brewer, and W.T. Swank. 1999. Simulated effects of reduced sulfur, nitrogen, and base cation deposition on soils and solutions in southern Appalachian forests. *Journal of Environmental Quality* 28:1336-1346.

Kratz, K.W., S.D. Cooper, and J.M. Melack. 1994. Effects of single and repeated experimental acid pulses on invertebrates in a high altitude Sierra Nevada stream. *Freshwater Biology* 32:161-183.

Lawrence, G.B., M.B. David, and W.C. Shortle. 1995 A new mechanism for calcium loss in forest floor soils. *Nature* 378:162-164.

Lawrence, G.B., M.B. David, S.W. Bailey, and W.C. Shortle. 1997. Assessment of calcium status in soils of red spruce forests in the northeastern United States. *Biogeochemistry* 38:19-39.

Leydecker, A., J.O. Sickman, J.M. Melack. 1999. Episodic lake acidification in the Sierra Nevada, CA. *Water Resources Research* 35(9):2793-2804.

Li, Z., and V.P. Aneja. 1992. Regional analysis of cloud chemistry at high elevations in the eastern United States. *Atmospheric Environment* 26A(11):2001-2017.

MacAvoy, S.E., and A.J. Bulger. 1995. Survival of Brook Trout (Salvelinus fontinalis) embryos and fry in streams of different acid sensitivity in Shenandoah National Park, USA. *Water, Air and Soil Pollution* 85: 445-450

Munson, R.K.1998. *Application of the NuCM Model to Noland Divide, White Oak Run, and Shaver Hollow for SAMI Phase I.* Final Report to SAMI, October, 1998. Tetra Tech Inc. Provo, UT.

Newman, K., and A. Dolloff. 1995. Responses of Blacknose Dace (Rhinichthys atratulus) and Brook Char (Salvelinus fontinalis) to acidified water in a laboratory stream. *Water, Air and Soil Pollution* 85: 371-376.

Nicholas, N.S., H. VanMiegroet, S.J. Zucker, and A.K. Rose. 1998. *A conceptual model to evaluate potential watershed nitrogen saturation in the Great Smoky Mountains. Proceedings of the 91st AWMA Annual Meeting and Exhibition*. June 14-18, 1998, San Diego, California.

Nodvin, S.C., H. Van Miegroet, S.E. Lindberg, N.S. Nicholas, and D.W. Johnson. 1995. Acidic deposition, ecosystem processes, and nitrogen saturation in a high elevation southern Appalachian watershed. *Water, Air and Soil Pollution* 85: 1647-1652.

Peterjohn, W.T., M.B. Adams, and F.S. Gilliam. 1996. Symptoms of nitrogen saturation in two central Appalachian hardwood forest ecosystems. *Biogeochemistry* 35: 507-522.

Shortle, W.C., K.T. Smith, R. Minocha, G.B. Lawrence, and M.B. David. 1997. Acidic deposition, cation mobilization, and biochemical indicators of stress in healthy red spruce. *Journal of Environmental Quality* 26:871-876.

Sickman, J.O., and J.M. Melak. 1998. Nitrogen and sulfate export from high elevation catchments of the Sierra Nevada, California. *Water, Air and Soil Pollution* 105: 217-226.

Sievering, H., D. Rusch, and L.Marquez. 1996. Nitric acid, particulate nitrate and ammonium in the continental free troposphere: nitrogen deposition to an alpine tundra ecosystem. *Atmospheric Environment* 30(14):2527-2537.

Smoot, J., B. Robinson, M. McCann, G. Harwell, and J. Shubzda. 2000. *Assessment of Stream Water Quality and Atmospheric Deposition Rates at Selected Sites in the Great Smoky Mountains National Park, 1991-1998*. Department of Civil and Environmental Engineering University of Tennessee Knoxville. Report prepared for the National Park Service cooperative agreement number 1443-CA-5460-98-006. (Amendment 3).

Stoddard, J.L., D.S. Jeffries, A. Lukewille, T.A. Clair, P.J. Dillon, D.T. Driscoll, M. Forsius, M. Johannessen, J.S. Kahl, J.H. Kellogg, A. Kemp, J. Mannio, D.T. Montaith, P.S. Murdoch, S. Patrick, A. Rebsdorf, B.L. Skjelkvale, M.P. Stainton, T. Traaen, H. vanDam, K.E. Webster, J. Wieting, and A. Wilander. 1999. Regional trends in aquatic recovery from acidification in North America and Europe. *Nature* 401:575-578.

Stoddard, J.L. 1995. Episodic acidification during snowmelt of high elevation lakes in the Sierra Nevada Mountains of CA. *Water, Air, and Soil P*ollution 85:353-358.

Thornton, F.C., J.D. Joslin, P.A. Pier, H. Neifeld, J.R. Seiler, and J.D. Hutcherson. 1994. Cloudwater and ozone effects upon high elevation red spruce: a summary of study results from Whitetop mountain, Virginia. *Journal of Environmental Quality* 23(6).

Vitousek, P.M., J.D. Aber, R.W. Howarth, G.E. Likens, P.A. Matson, D.W. Schindler, W.H. Schlesinger, and D.G. Tilman. 1997. Human alteration of the global nitrogen cycle: Sources and consequences. *Ecological Applications* 7(3):737-750.

Weathers, K.C., G.E. Likens, F.H. Bormann, J.S. Eaton, W.B. Bowden, J.L. Andersen, D.A. Cass, J.N. Galloway, W.C. Keene, K.D. Kimball, P. Huth, and D. Smiley. 1986. A regional acidic cloud/fog water event in the eastern U.S. *Nature* 319(6055):657-658.

Webb, J.R., B.J. Cosby, F.A. Deviney Jr., D.N. Eshleman, and J.N. Galloway. 1995. Change in the acid-base status of an Appalachian mountain catchment following forest defoliation by the gypsy moth. *Water, Air and Soil Pollution* 85:535-540.

Williams, M.W., R.C. Bales, A.D. Brown, and J.M. Melack. 1995. Fluxes and transformations of nitrogen in a high-elevation catchment, Sierra Nevada. *Biogeochemistry* 28:1-31.

Williams, M.W., J.S. Baron, N. Caine, R. Sommerfeld, and R. Sanford. 1996. Nitrogen saturation in the Rocky Mountains. *Environmental Science and Technology* 30.

Williams M.W., and K.A. Tonnessen. 2000. Critical loads for inorganic nitrogen deposition in the Colorado Front Range, USA. *Ecological Applications* 10(6):1648-1665.

Williams, M.R., and J.M. Melack. 1997. Atmospheric deposition, mass balances, and processes regulating streamwater solute concentrations in mixed-conifer catchments of the Sierra Nevada, California. *Biogeochemistry* 37:111-144.

Wolford and Bales. 1996. Hydrochemical modeling of Emerald Lake watershed, Sierra Nevada, CA: Sensitivity of stream chemistry to changes in fluxes and model parameters. *Limnological Oceanography* 41(5):947-954.

% of Western Virginia Streams with ANC<0 At Various Modeled Reductions in Deposition

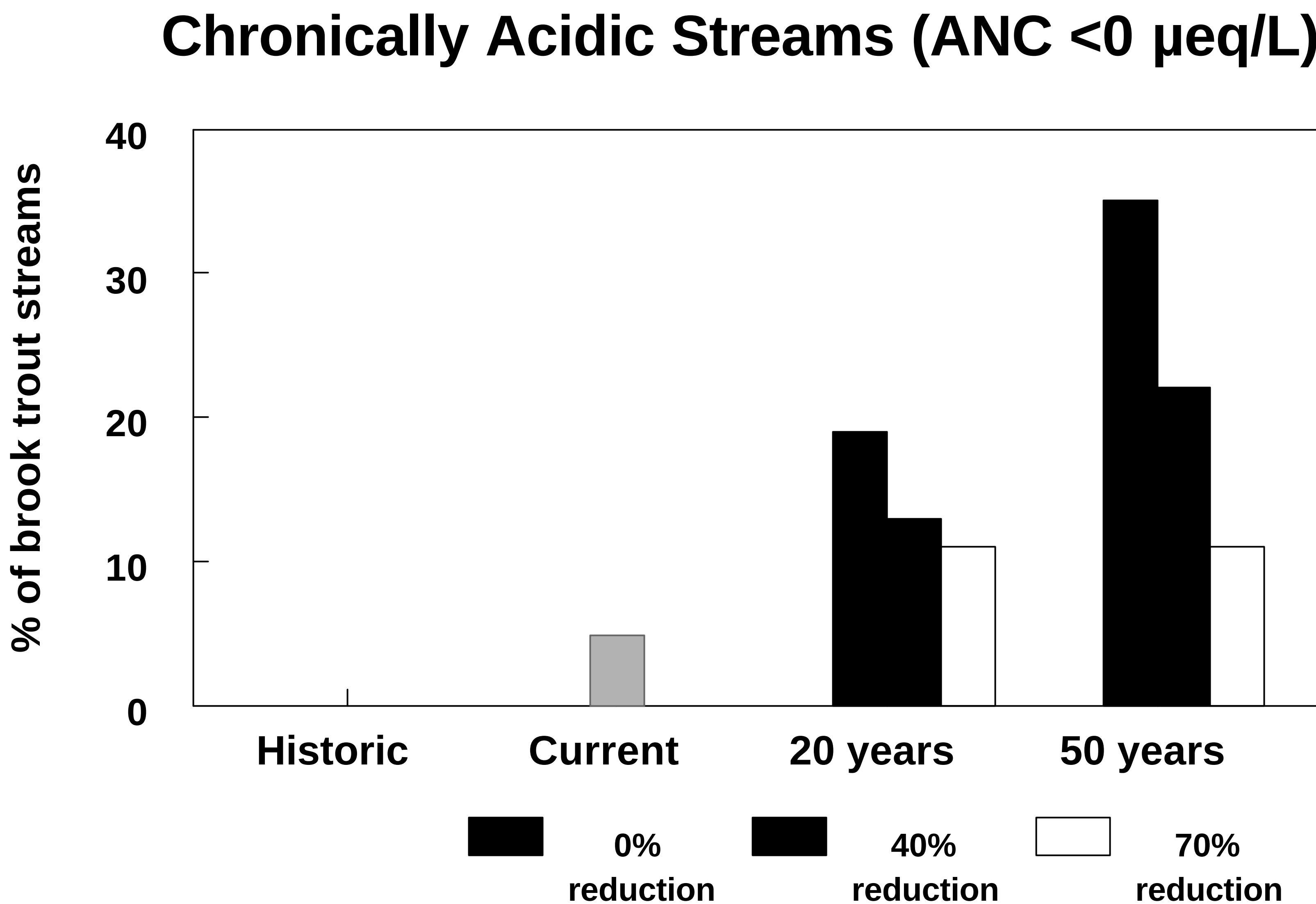


Figure 1.

From Bulger et al 2000b (figure 2c)

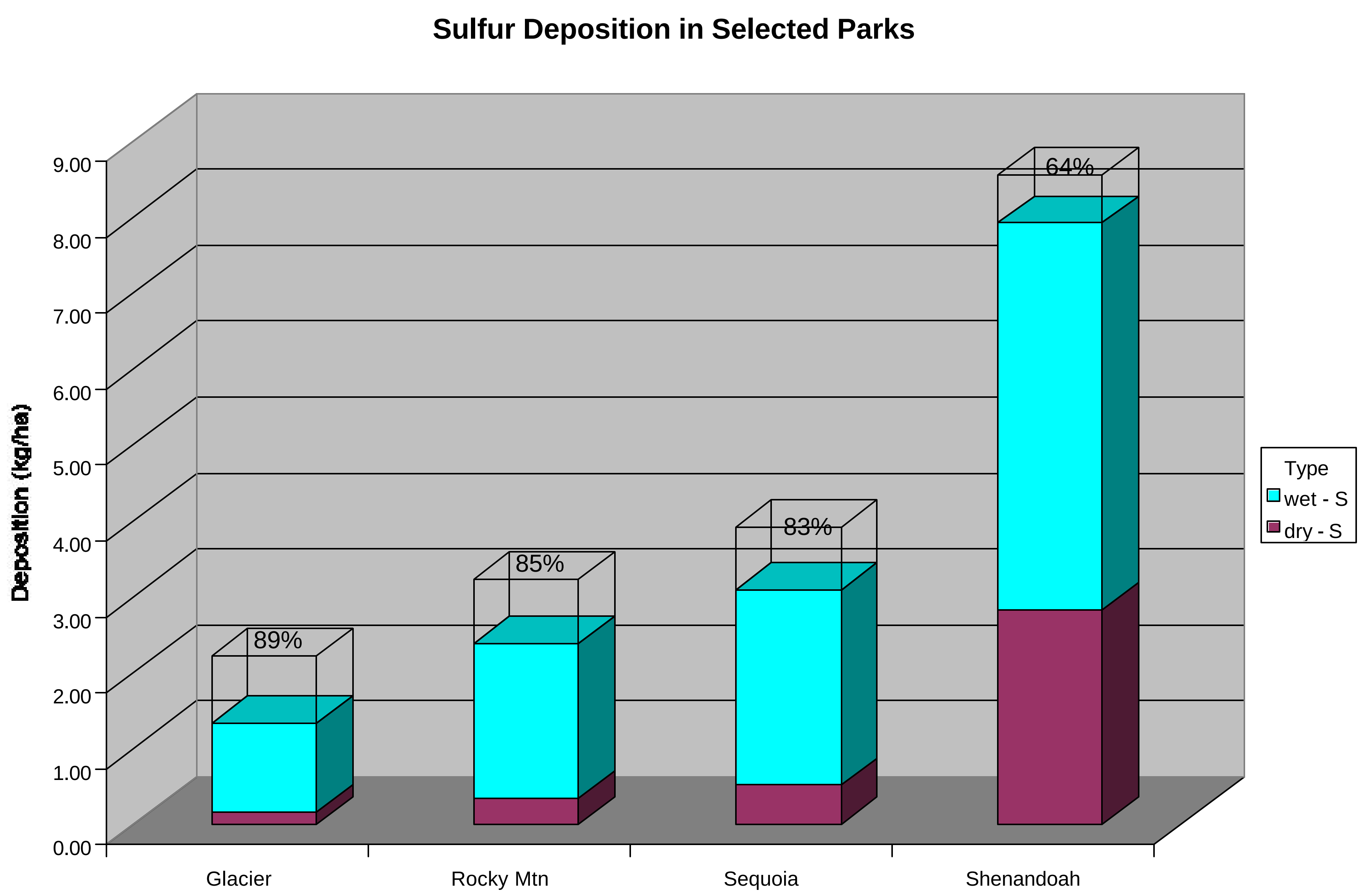
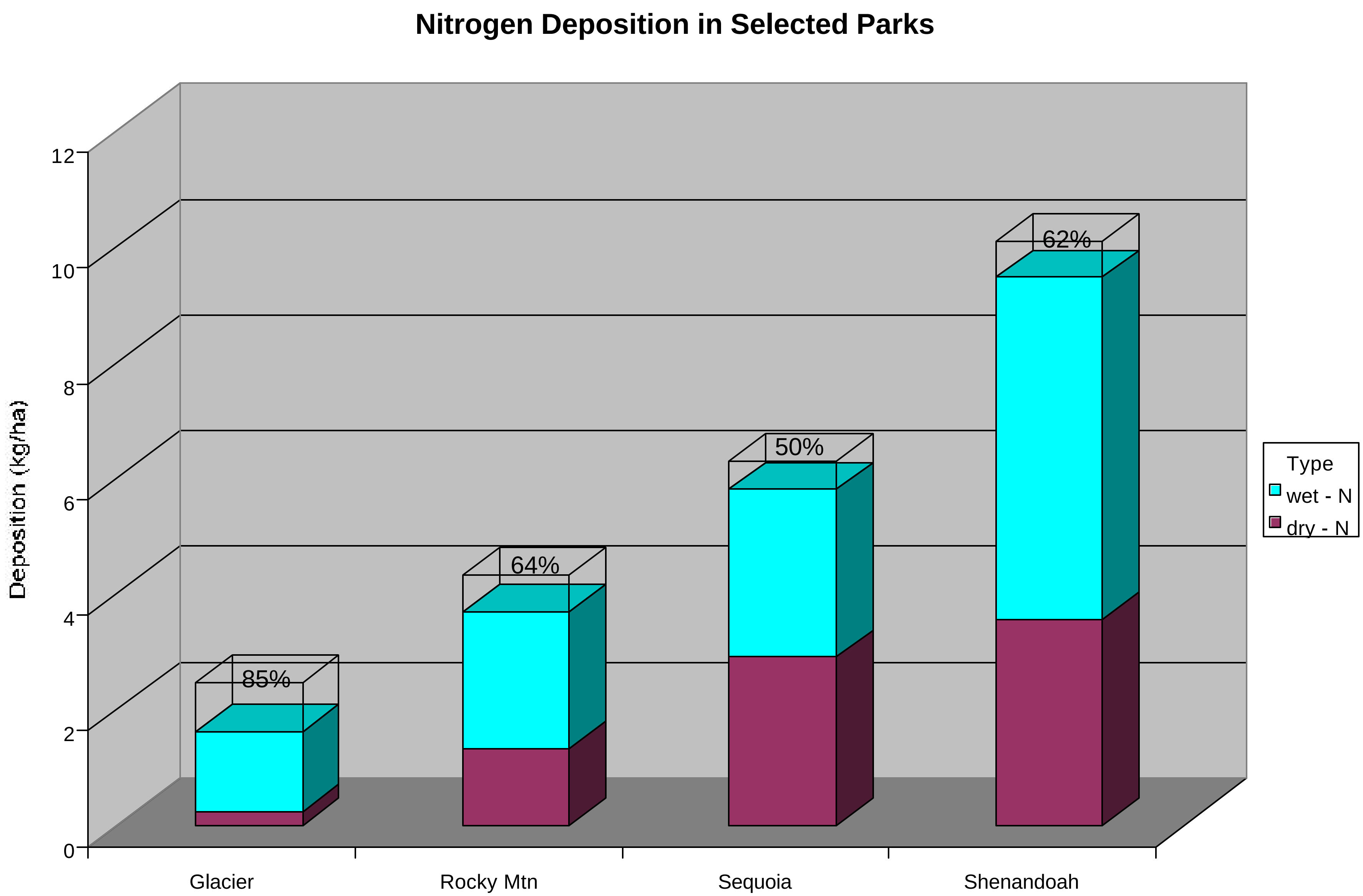

Sulfur Deposition in Selected Parks
Deposition (kg/ha)
9.00
8.00
7.00
6.00
5.00
4.00
3.00
2.00
1.00
0.00
89%
85%
83%
64%
Glacier
Rocky Mtn
Sequoia
Shenandoah
Type
wet - S
dry - S

Figure 2.



Nitrogen Deposition in Selected Parks
Deposition (kg/ha)
12
10
8
6
4
2
0
85%
64%
50%
62%
Glacier
Rocky Mtn
Sequoia
Shenandoah
Type
wet - N
dry - N

Figure 3.

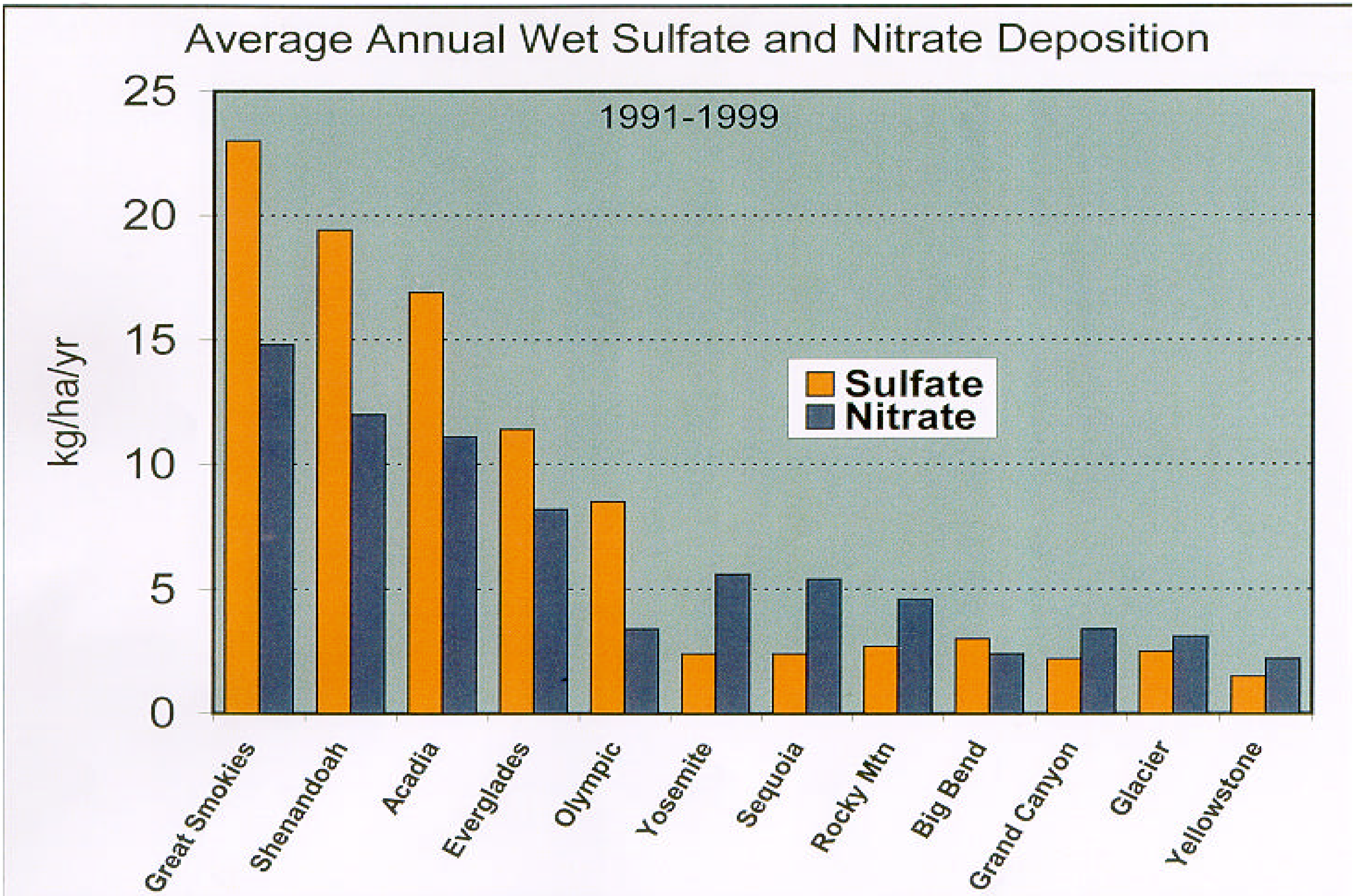
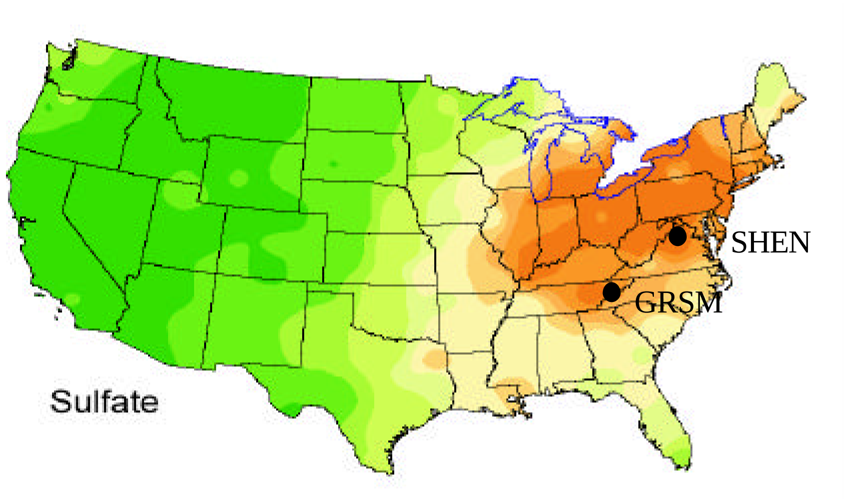

Average Annual Wet Sulfate and Nitrate Deposition
1991-1999
kg/ha/yr
25
20
15
10
5
0
Sulfate
Nitrate
Great Smokies
Shenandoah
Acadia
Everglades
Olympic
Yosemite
Sequoia
Rocky Mtn
Big Bend
Grand Canyon
Glacier
Yellowstone

Figure 4.

Sulfate Deposition 1985-1989



Sulfate Deposition 1995-1999

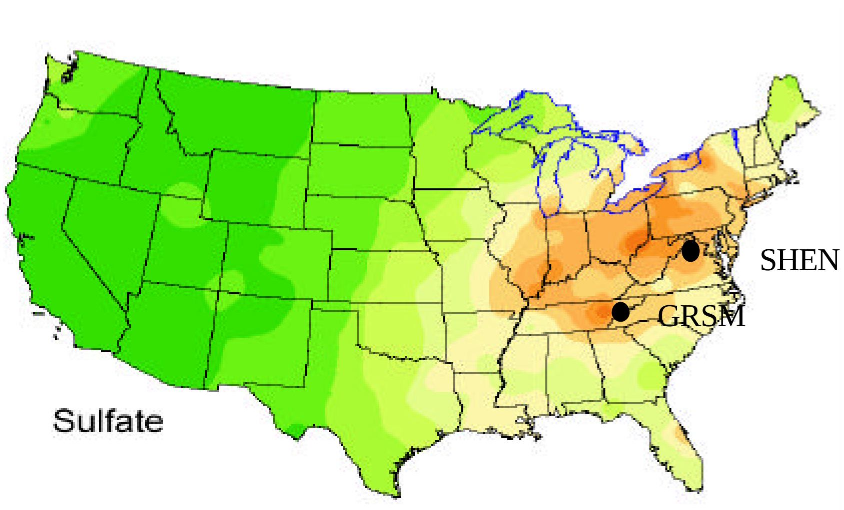


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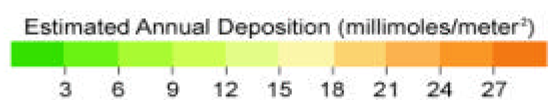
Figure 5.



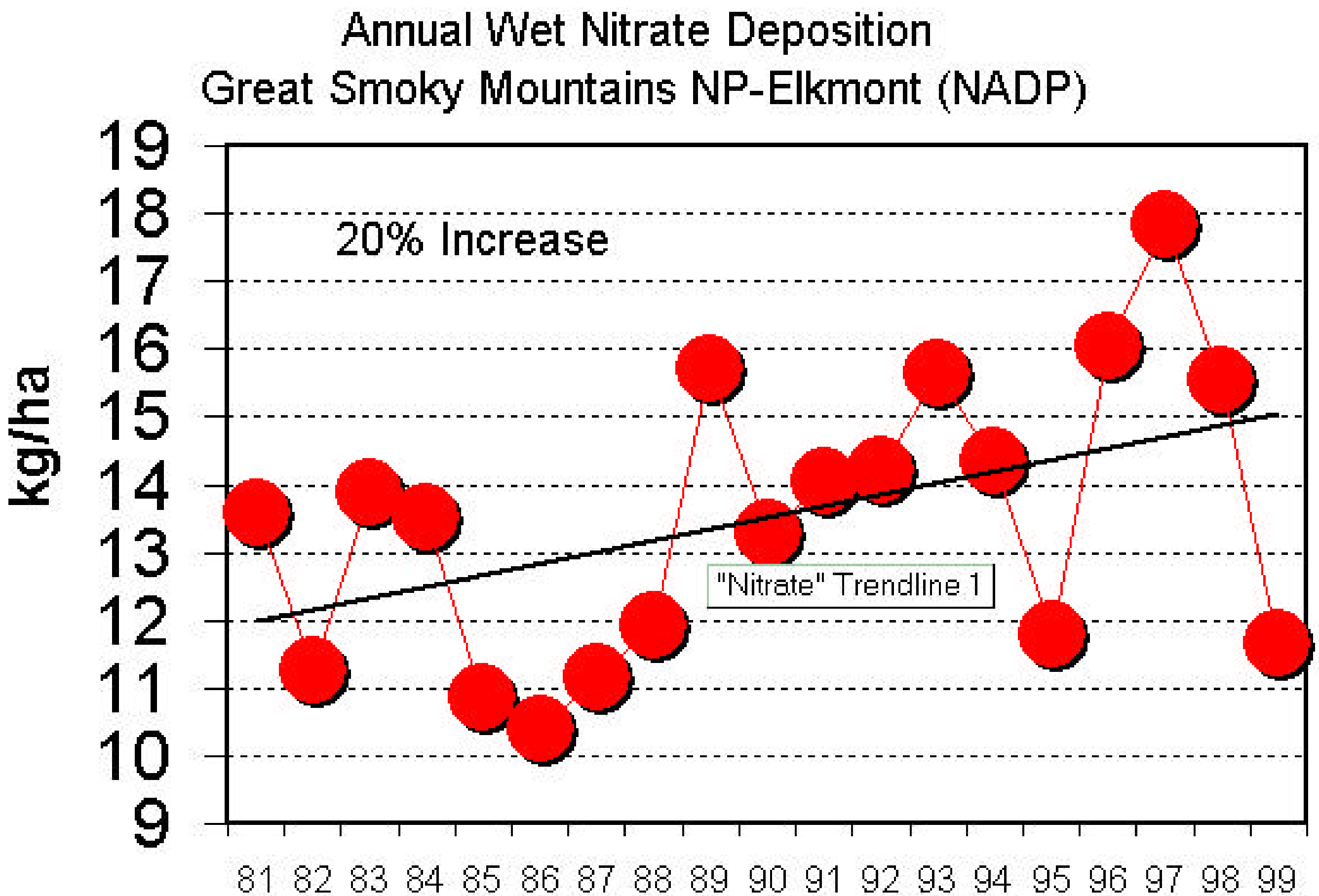

Annual Wet Nitrate Deposition
Great Smoky Mountains NP-Elkmont (NADP)
kg/ha
19
18
17
16
15
14
13
12
11
10
9
20% Increase
"Nitrate" Trendline 1
81 82 83 84 85 86 87 88 89 90 91 92 93 94 95 96 97 98 99

Figure 6.

Great Smoky Mountains National Park Stream Nitrate

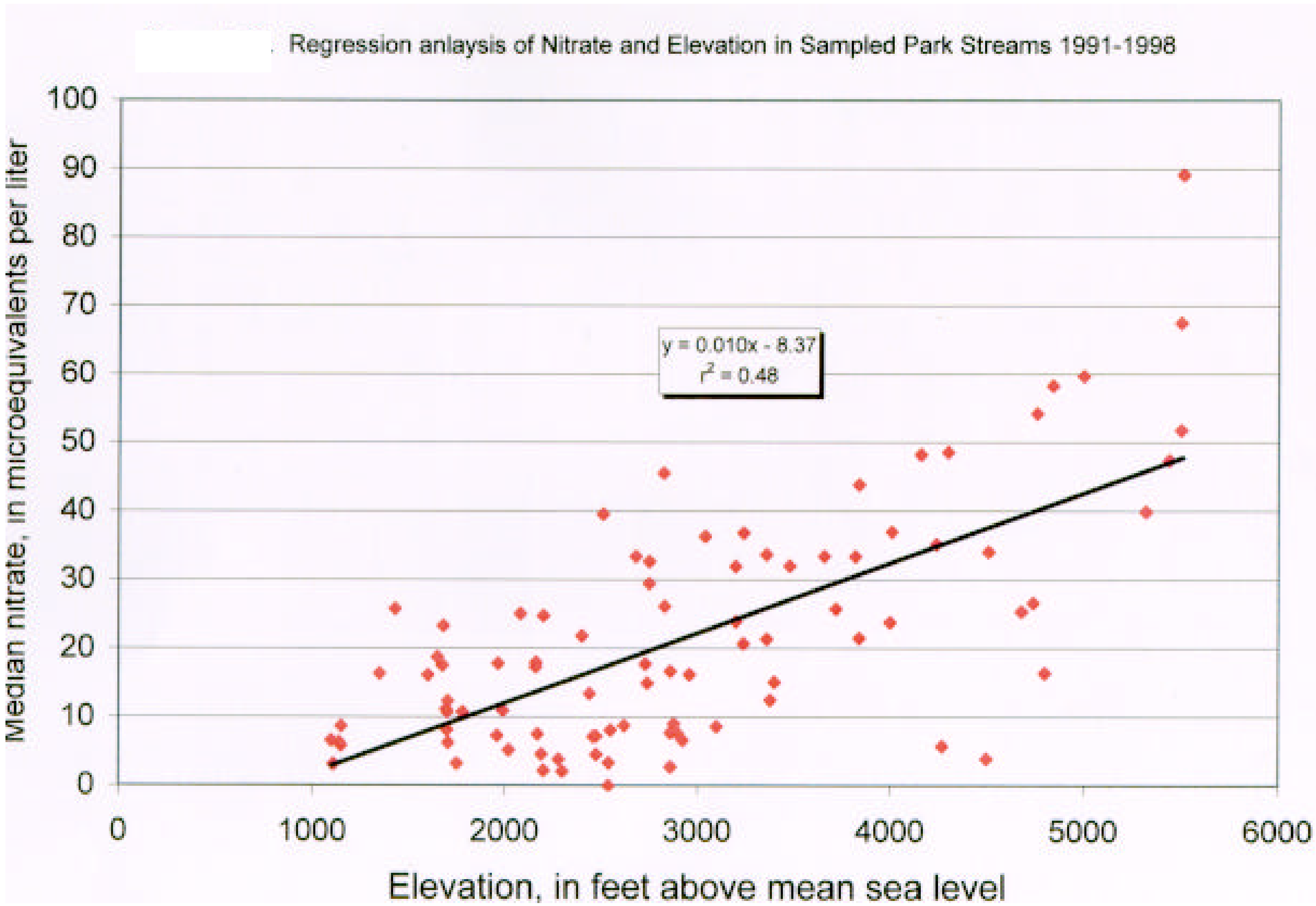


Figure 7.

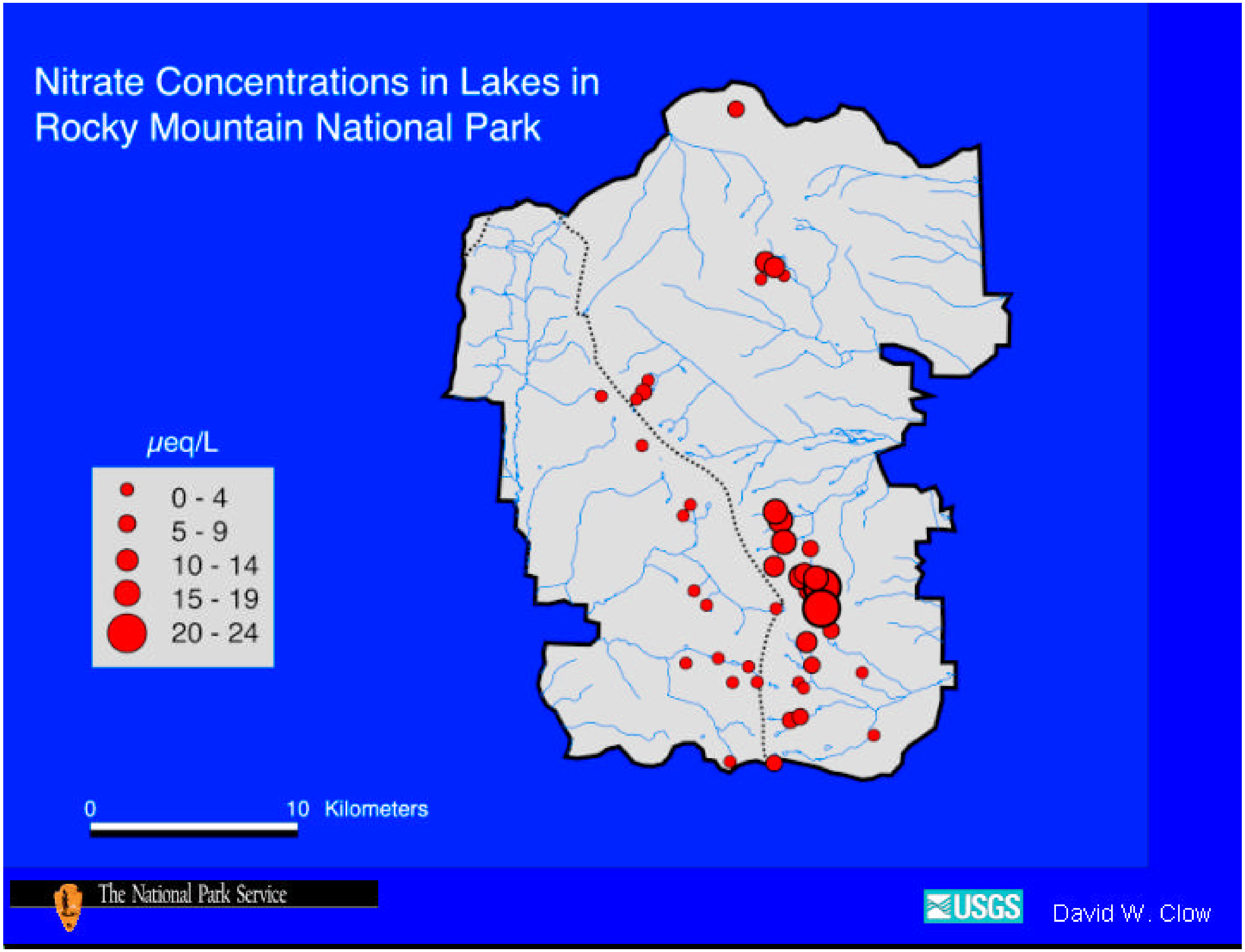

Nitrate Concentrations in Lakes in
Rocky Mountain National Park
µeq/L
0 - 4
5 - 9
10 - 14
15 - 19
20 - 24
0
10 Kilometers
The National Park Service
USGS
David W. Clow

Figure 8.

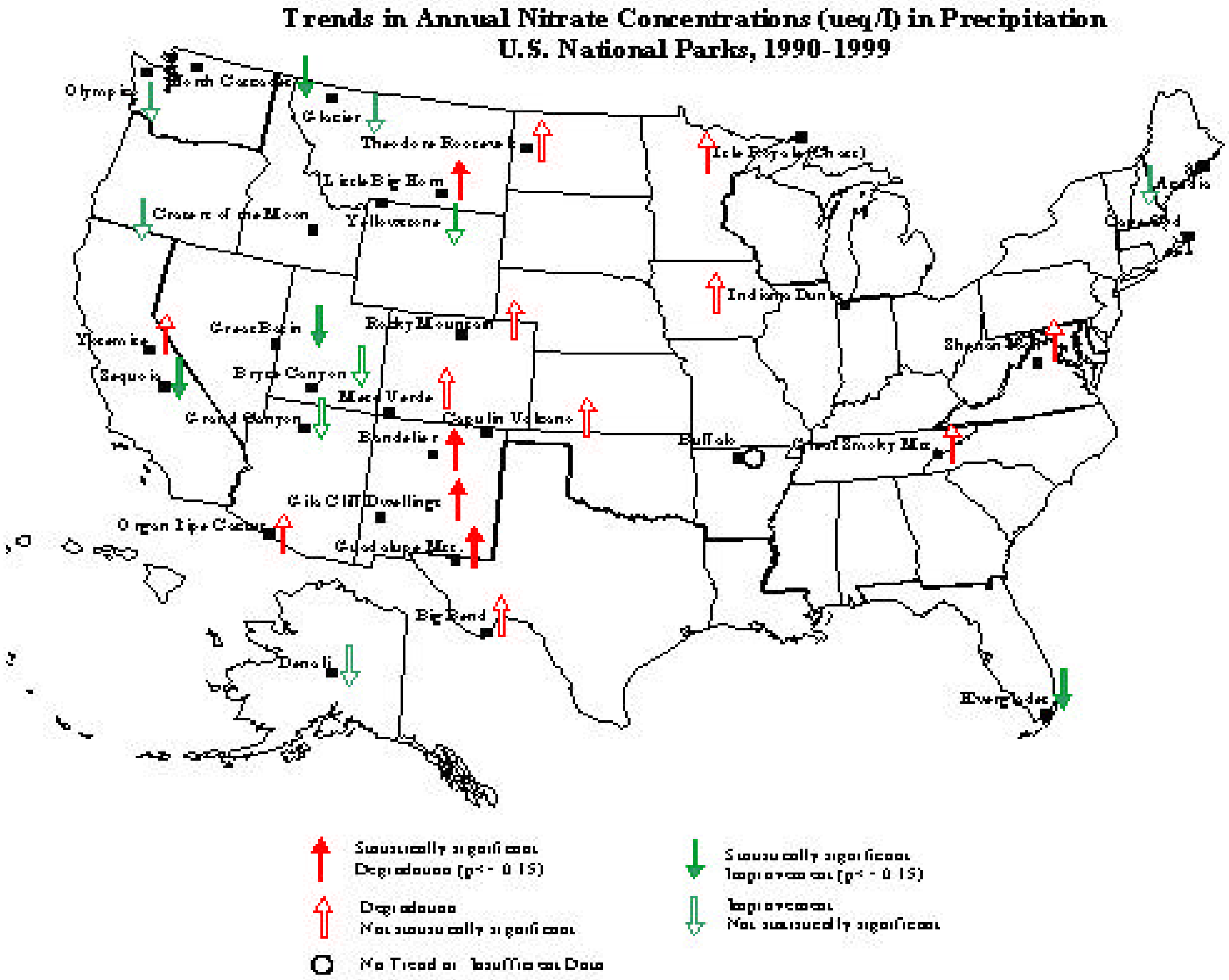


Figure 9.

Prepared by NPS for GPRA reporting: 10 yr increments in trends

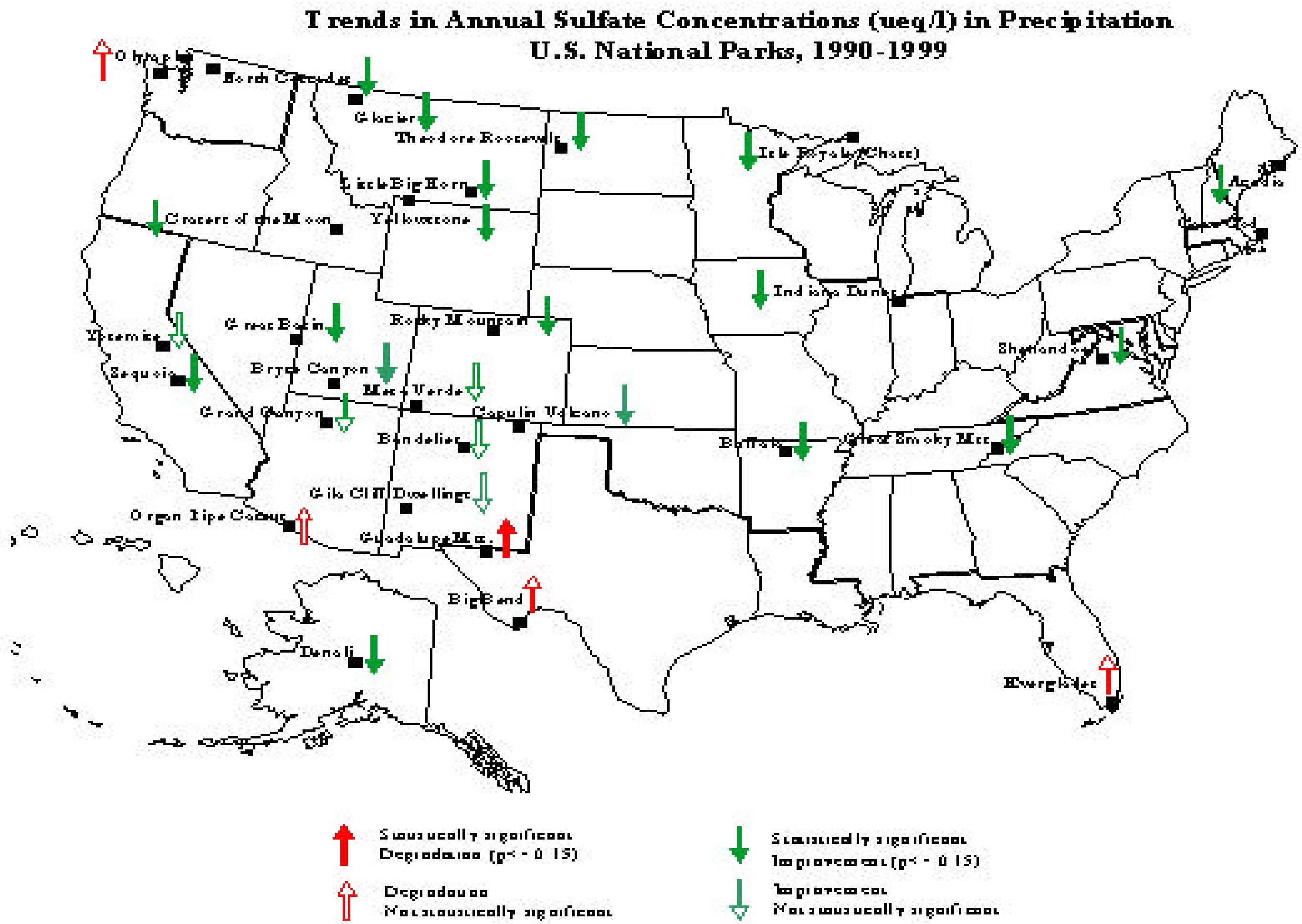


Figure 10.

Prepared by NPS for GPRA reporting: 10 yr increments in trends

Nitrate Deposition

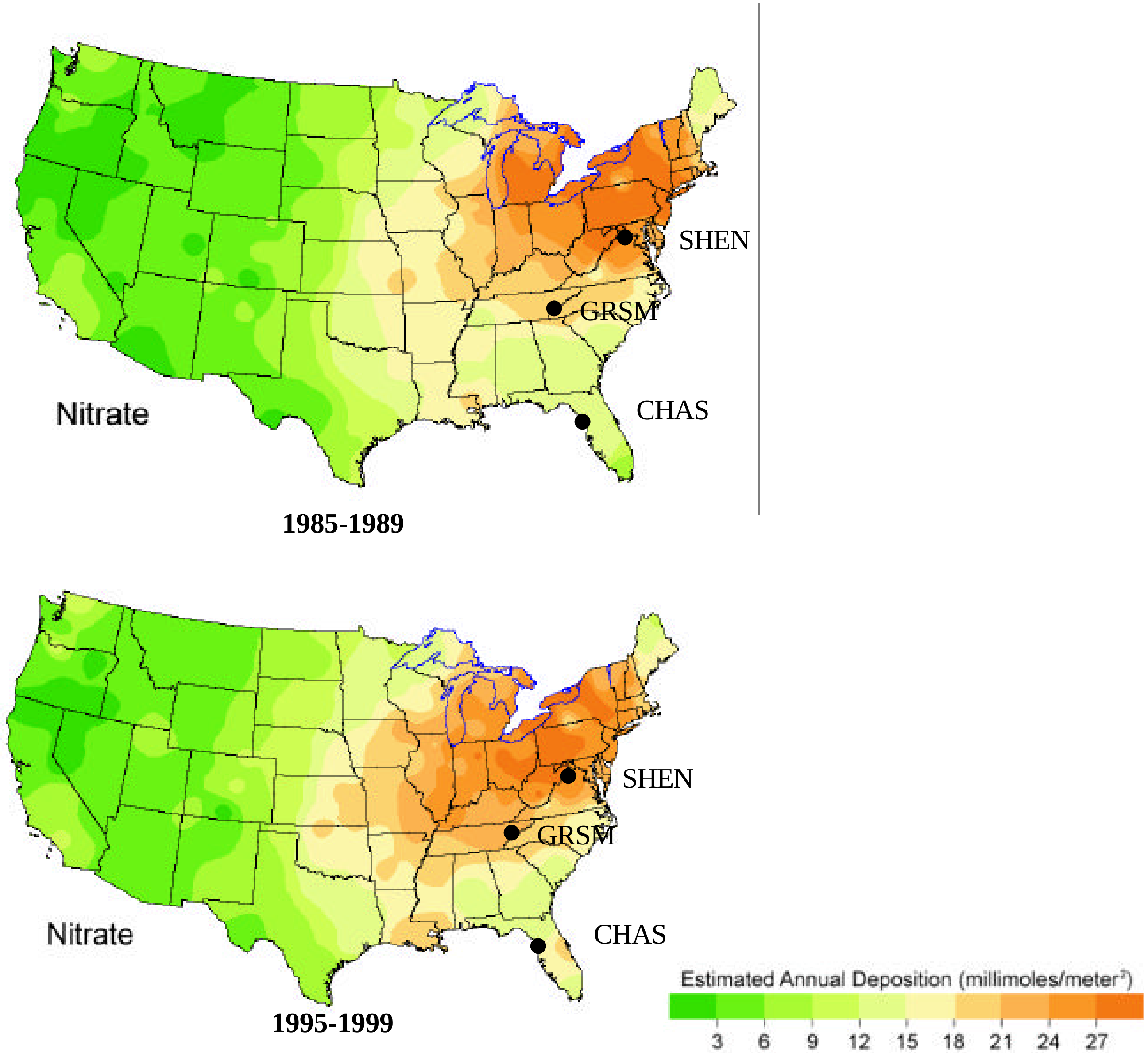


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Figure 11.

Nitrate ion concentration, 1998

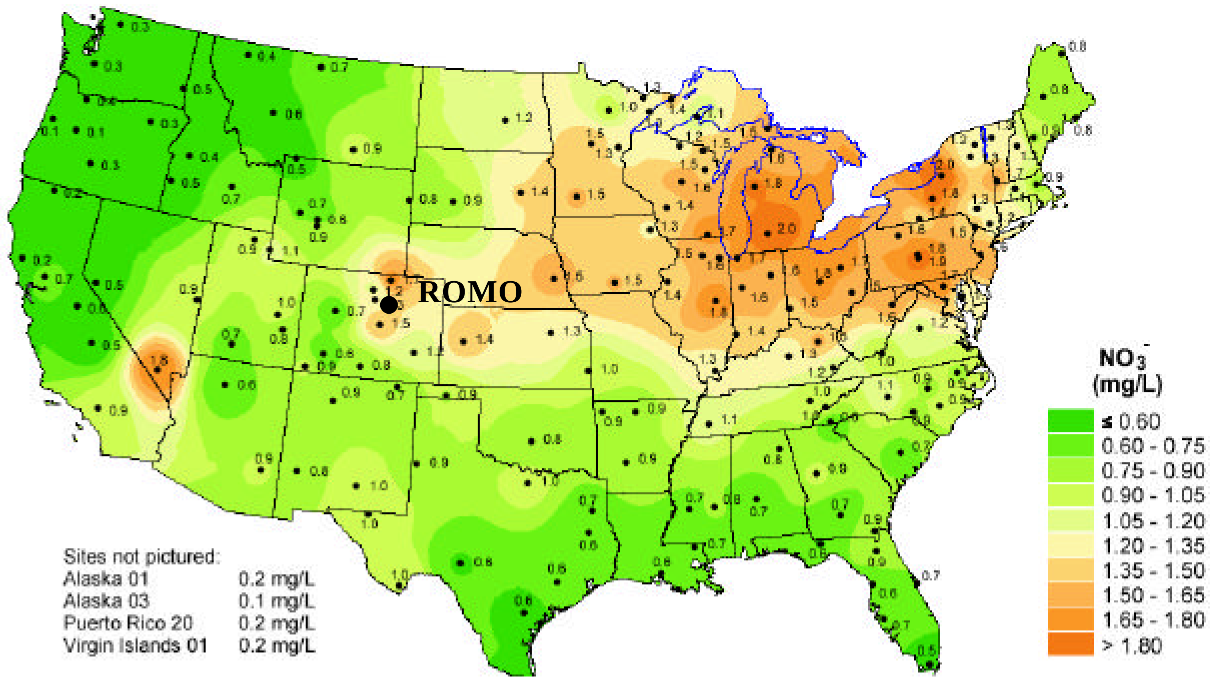
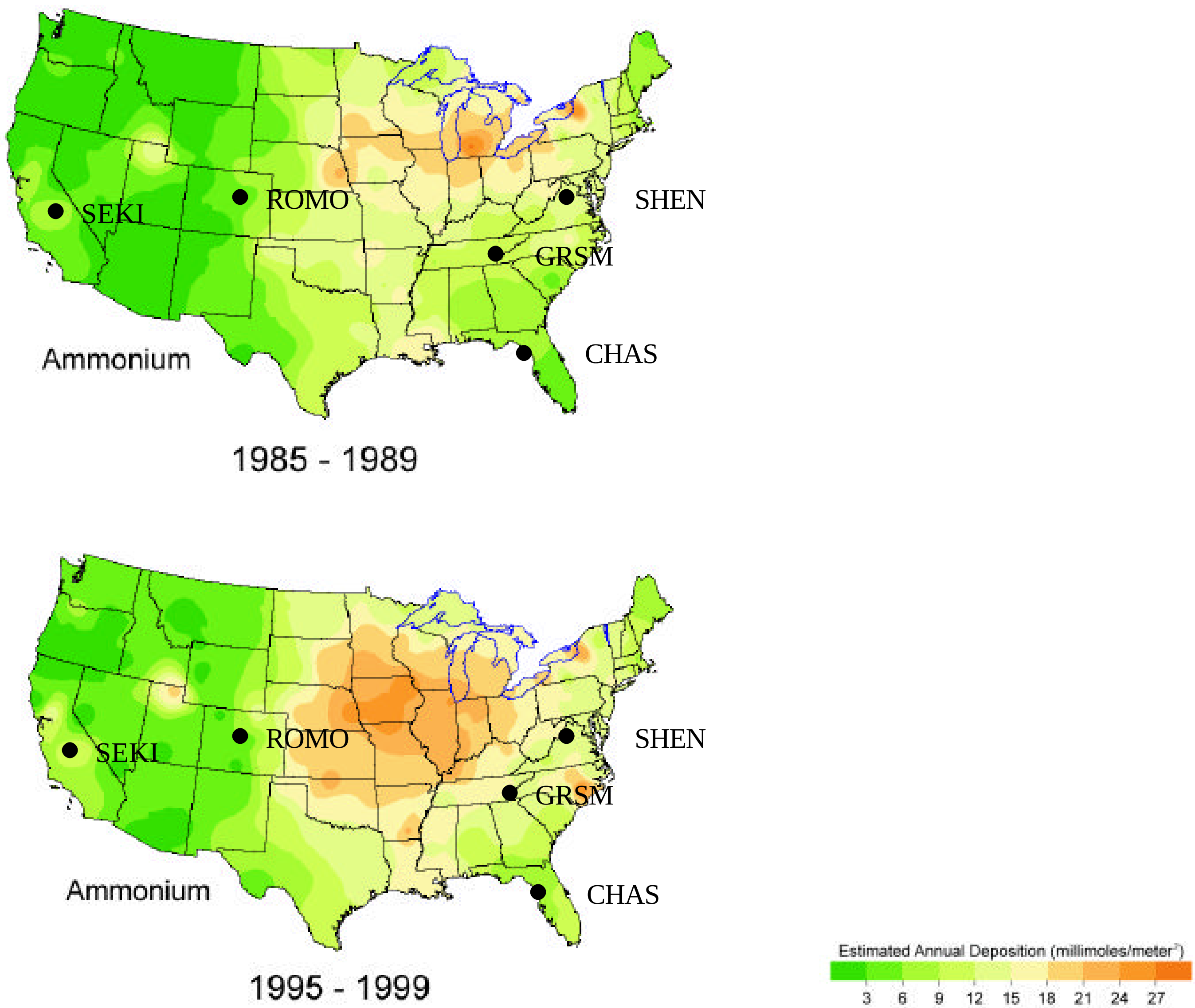


Figure 12.

Ammonium Deposition



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and Private Research Organizations

Figure 13.