



Air Quality Related Values (AQRVs) for Sierra Nevada Network (SIEN) Parks

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

Natural Resource Report NPS/SIEN/NRR—2016/1187



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/SIEN/NRR—2016/1187

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April 2016

U.S. Department of the Interior
National Park Service
Natural Resource Stewardship and Science
Fort Collins, Colorado

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Please cite this publication as:

Sullivan, T. J. 2016. Air quality related values (AQRVs) for Sierra Nevada Network (SIEN) parks: Effects from ozone; visibility reducing particles; and atmospheric deposition of acids, nutrients and toxics. Natural Resource Report NPS/SIEN/NRR—2016/1187. National Park Service, Fort Collins, Colorado.

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Summary

This report describes the Air Quality Related Values (AQRVs) of the Sierra Nevada Network (SIEN). AQRVs are those resources sensitive to air quality and include streams, lakes, soils, vegetation, fish and wildlife, and visibility. The SIEN parks that are included in the NPS Inventory and Monitoring (I&M) Program and discussed in this report are jointly-managed Sequoia and Kings Canyon National Parks (SEKI), Yosemite National Park (YOSE), and Devil's Postpile National Monument (DEPO). SEKI and YOSE are Class I air quality areas, giving them a heightened level of protection against harm caused by poor air quality under the Clean Air Act (CAA). DEPO is a Class II area.

Sullivan et al. (2011a, 2011b) and Kohut (2007) conducted risk assessments for acidification, eutrophication, and ozone (O_3) for all of the SIEN parks; their results are described in this report. This report also describes air pollutant emissions and air quality in the SIEN, 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 Chapters 1-2 of “Air quality related values (AQRVs) in national parks: Effects from ozone; visibility reducing particles; and atmospheric deposition of acids, nutrients and toxics” (Sullivan 2016).

Urban and agricultural emissions affect air quality in California's national parks, particularly parks in the Sierra Nevada. The San Joaquin Valley, upwind of the SIEN parks, is one of the most polluted areas in California and is a primary source of air pollutants transported to these parks (Lin and Jao 1995). The Central Valley, with a population of 6.5 million, has been the fastest growing region of California. Wildland fires, a common occurrence in this region, are also large contributors to air pollution in the parks (McMeeking et al. 2006).

Sulfur and N pollutants can cause acidification of streams, lakes, and soils. The levels of N deposition received in high-elevation portions of SEKI and YOSE have contributed to some episodic acidification of surface waters during snowmelt and rain storms (Sickman and Melack 1989). Slight chronic acidification may also have occurred in the most acid-sensitive aquatic systems (Sickman and Melack 1989). Such effects on water chemistry, though small in magnitude, may have had subtle long-term effects on aquatic biota.

Nitrogen pollutants can also cause undesirable enrichment of natural ecosystems, leading to changes in plant species diversity and soil nutrient cycling. Certain lichen species now found in YOSE are suggestive of N pollution, and modeled N deposition in all SIEN parks exceeds levels known to harm natural diversity in lichen communities and herbaceous plant and shrub communities (Fenn et al. 2011b). In high elevation lakes in the eastern Sierra Nevada, increased N from deposition has induced changes in diatom communities from species adapted to low N conditions to species typical of more nutrient-rich, disturbed lakes. To date, these changes have not been observed in SIEN park lakes (cf., Sickman and Bennett 2011).

Ozone pollution can harm human health, reduce plant growth, injure foliage, and render sensitive plant species more vulnerable to drought and other stressors (Grulke et al. 1998, Grulke and Balduman 1999). All parks in the SIEN are located in counties designated as nonattainment for the O₃ National Ambient Air Quality Standard (NAAQS). Sequoia and Kings Canyon NPs have O₃ health advisory programs that alert visitors when the air is expected to be unhealthy because of high O₃ levels. Parts of SEKI, in particular, experience some of the worst air quality in the National Park system (Panek et al., 2012). Vegetation at SEKI has exhibited among the most severe effects of O₃ in California outside the Los Angeles Basin, with more documented impacts than at any other western national park (Bytnerowicz et al. 2008). Ozone-induced foliar injury in ponderosa pine (*Pinus ponderosa*) and Jeffrey pine (*Pinus jeffreyi*) has been widespread and pronounced in the western regions of SEKI and was present to a lesser extent in YOSE. Foliar injury has also been documented in giant sequoia (*Sequoiadendron giganteum*) seedlings. Reduced foliar biomass and tree growth at some locations suggest that ecosystem productivity may have been affected by chronic, long-term exposure to elevated levels of O₃ in the mixed conifer zone.

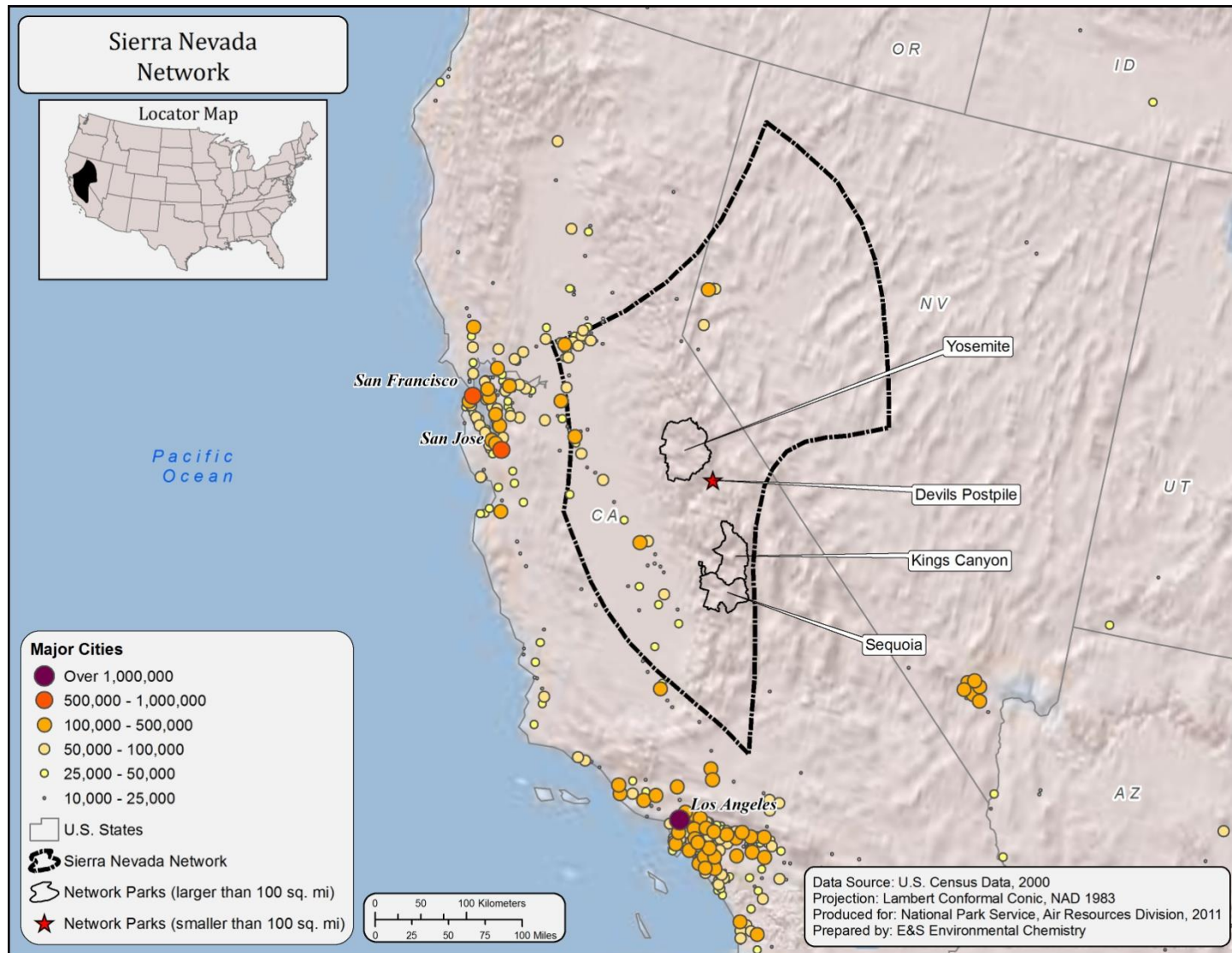
Particulate pollution can cause haze, reducing visibility even at levels well below the NAAQS for fine particulate matter (PM_{2.5}; Pitchford and Malm 1994). Visibility in SIEN parks is often reduced substantially from estimated natural background conditions.

Pesticides are used heavily in California's agricultural valleys, especially the San Joaquin Valley. Some are highly volatile and are transported through the atmosphere to sites in the Sierra Nevada, including within SEKI and YOSE. Other toxic substances, including mercury (Hg), are also deposited in national park ecosystems in the SIEN. Current use pesticides (CUPs) were found to be especially prevalent in Sequoia NP, as compared with other park lands in the western United States (Landers et al. 2008).

Background

There are four parks in the SIEN: Devil's Postpile National Monument (DEPO), Yosemite National Park (YOSE), and Sequoia and Kings Canyon national parks, which are jointly managed and referred to as SEKI; they are combined for most analyses in this chapter. The SEKI parks and YOSE are all larger than 100 square miles. The one smaller park is DEPO. Larger parks generally have more available data with which to evaluate air pollution sensitivities and effects. In addition, the larger parks generally contain more extensive resources in need of protection against the adverse impacts of air pollution.

There are several human population centers larger than 100,000 people within the SIEN region. There are also several large population centers on the perimeter of the SIEN boundary, including San Francisco, San Jose, and Sacramento. Map 1 shows the network boundary along with locations of each park and population centers with greater than 10,000 people. The two areas of California that show the most severe air quality problems have been the South Coast and the San Joaquin Valley (Suarez-Murias et al. 2009).



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

The Sierra Nevada region has elevated concentrations of ozone (O_3) and nitrogen (N) air pollutants (Bytnerowicz et al. 1999, Bytnerowicz and Fenn 1996). Serious concerns have been raised regarding effects on natural resources in SEKI and YOSE due to air pollutants emitted in the San Francisco Bay area and the San Joaquin Valley (Bytnerowicz et al. 2002) coupled with high resource sensitivity.

Bytnerowicz et al. (2002) characterized N, sulfur (S), and O_3 air pollutants along an elevational gradient in Sequoia NP. They found significant declines in atmospheric concentrations of O_3 , nitric acid (HNO_3), ammonia (NH_3), and sulfur dioxide (SO_2) with increasing elevation and distance from pollution source areas. In contrast, the highest concentrations of particulate nitrate (NO_3^-) and ammonium (NH_4^+) were observed at mid-elevation, likely due to generation of NH_4NO_3 during atmospheric transport from pollution source areas.

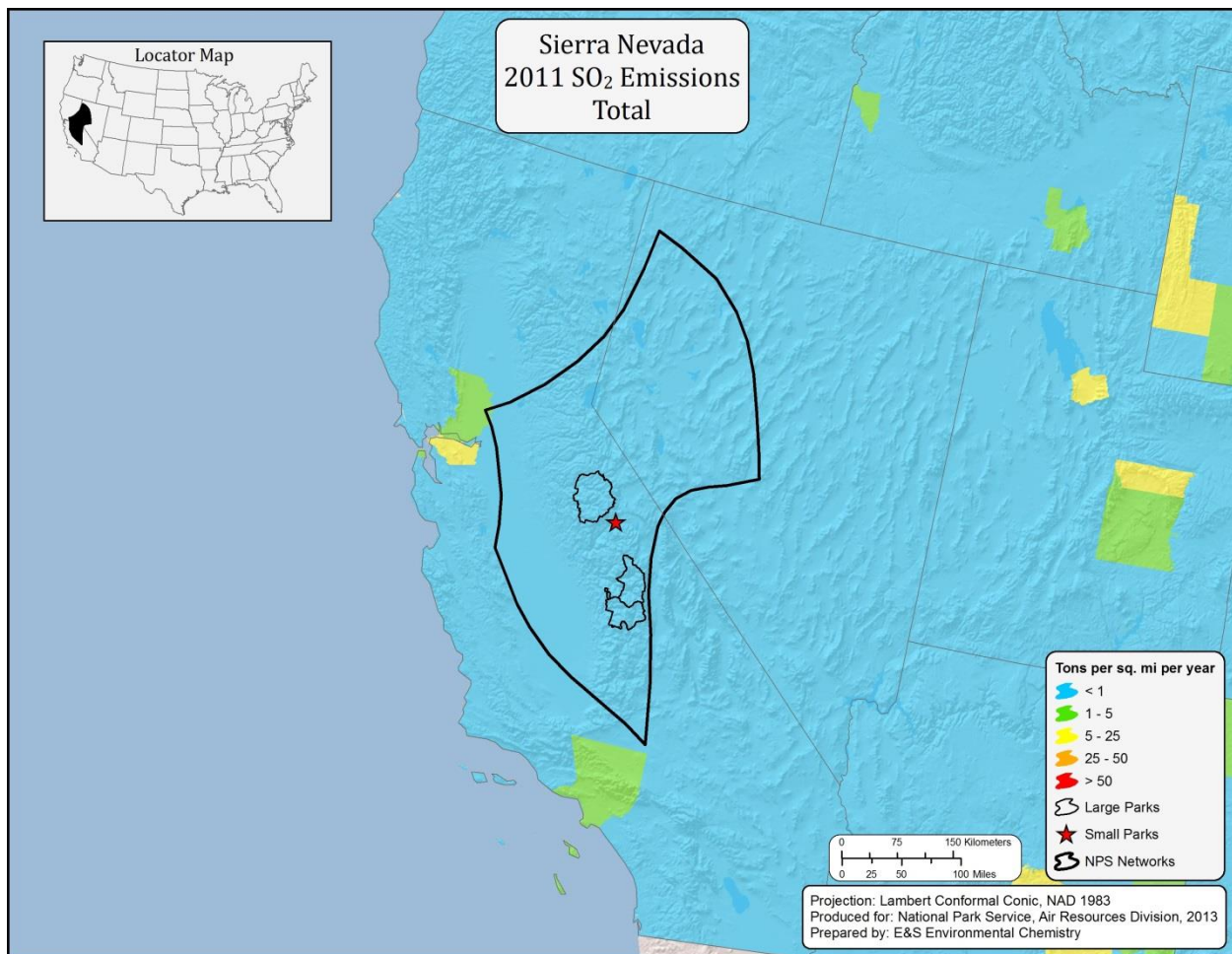
Atmospheric Emissions and Deposition

Because the prevailing winds are from the west and northwest, many of California's national parks and Class I areas, including those located in the Sierra Nevada, are downwind of some of the major urban and agricultural areas of the state. California is the most populous state in the nation, with major population centers located along the Pacific coast and in the Sacramento and San Joaquin valleys. The Central Valley of California is also one of the most intensively cultivated agricultural regions of the United States. Air pollution is an important concern in portions of the park lands in the SIEN that are in proximity to major emissions sources.

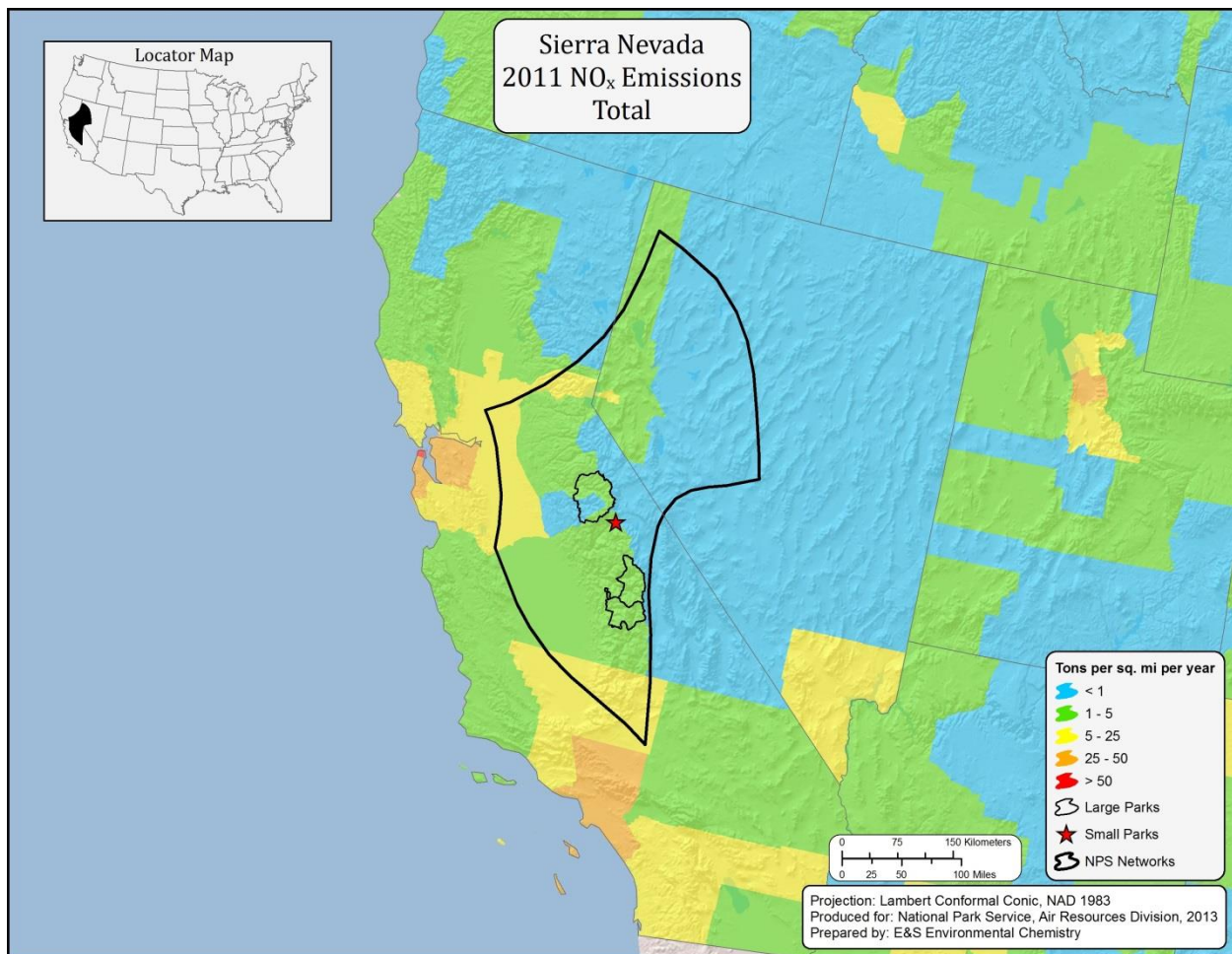
Sulfur dioxide (SO₂) emissions have been low in California for several decades and do not currently pose a significant concern for parks in the SIEN. County-level SO₂ emissions within the SIEN region were mostly less than 1 ton per square mile in 2002, with somewhat higher emissions in the westernmost portion of the region and in the San Francisco Bay area. Most of the point source emissions of SO₂ identified by Sullivan et al. (2011b) near the SIEN parks were relatively small (less than 5,000 tons per year) and located to the west of the parks, within about 100 miles of the coast.

County-level emissions near the SIEN, 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 N (NO_x), and reduced N (NH₃), respectively. Counties in the vicinity of SIEN parks had low SO₂ emissions (< 1 ton per square mile per year [ton/mi²/yr]; Map 2). Oxidized N emissions were higher, mostly in the range of 1 to 5 tons/mi²/yr (Map 3). Emissions of NH₃ near SIEN parks were higher, but were mostly less than 8 tons/mi²/yr (Map 4).

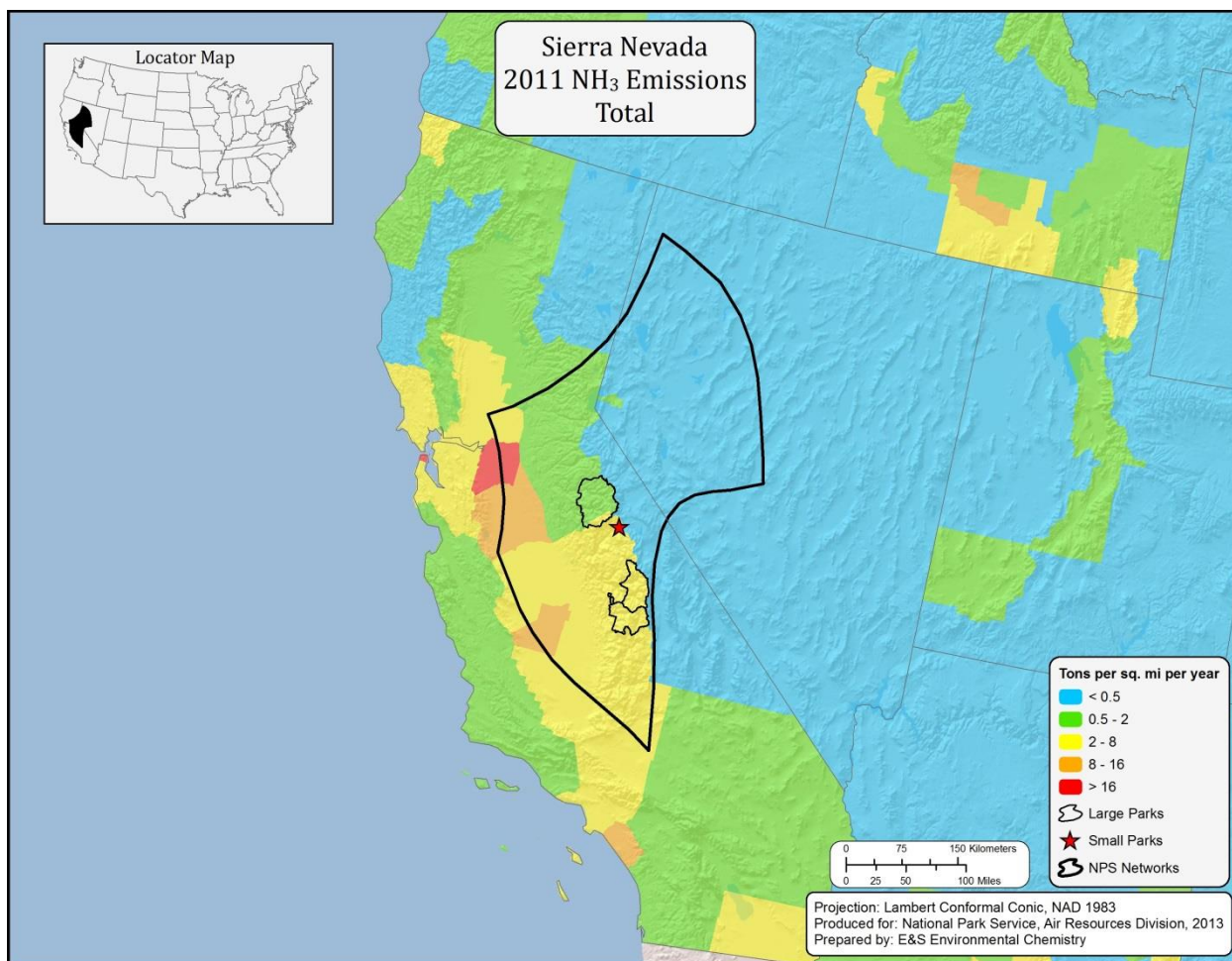
Nitrogen emissions and deposition are a more substantial concern for SIEN parks. County-level N emissions near the network generally ranged from less than 1 ton/mi²/yr around YOSE to 20 tons/mi²/yr near SEKI. Most sources are mobile or areal. There were very few point sources of N of any magnitude in the SIEN region. Most emissions of O₃ precursors (i.e., NO_x and volatile organic compounds [VOCs]) come from source areas in the South Coast, San Francisco Bay Area, and San Joaquin Valley (<http://www.epa.gov/ttnchie1/trends/>). These emissions are mainly from motor vehicles, with other significant sources of N from fossil-fueled power plants and of reactive organic gasses from cleaning and surface coatings and solvent evaporation. Additionally, the land in the western portion of the SIEN region is a mix of row crops, pasture/hay, and developed areas which are potential sources of air pollutants (especially NH₃, O₃ and pesticides) to the parks in the SIEN. Southern airsheds on the west side of the Sierra Nevada (including those in and upwind of SEKI and YOSE) experience elevated N emissions and deposition, especially during summer (<http://epa.gov/castnet/javaweb/index.html>).



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



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



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

Total modeled S deposition in 2002 was less than 2 kilograms/hectare/year (kg/ha/yr) throughout virtually the entire SIEN region (Sullivan et al. 2011b). Estimated total N deposition in 2002 ranged from less than 2 kg N/ha/yr to higher than 10 kg N/ha/yr.

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

Atmospheric S and N deposition levels have increased at all SIEN parks since 2002, based on TDEP estimates (Table 1). Increases in total S deposition over the previous decade for the parks in this network were typically about 20%. Estimated total N deposition also increased over that same time period, and the increases were larger than those for S. Oxidized N deposition was relatively stable, but reduced N increased, in most cases approximately doubling since the monitoring period 2000-2002.

Total S deposition in and around the SIEN estimated by TDEP for the period 2010-2012 was low (< 2 kg S/ha/yr) at park locations within the network area (Map 5). Oxidized inorganic N deposition for the period 2010-2012 was in the range of 2 to 5 kg N/ha/yr throughout the park lands within the SIEN (Map 6). Most areas received less than 5 kg N/ha/yr of reduced inorganic N from atmospheric deposition during this same period (Map 7); reduced N deposition was higher in parts of SEKI. Total N deposition was in the range of 5 to 10 kg N/ha/yr at most park locations (Map 8); parts of SEKI were estimated to have received higher amounts.

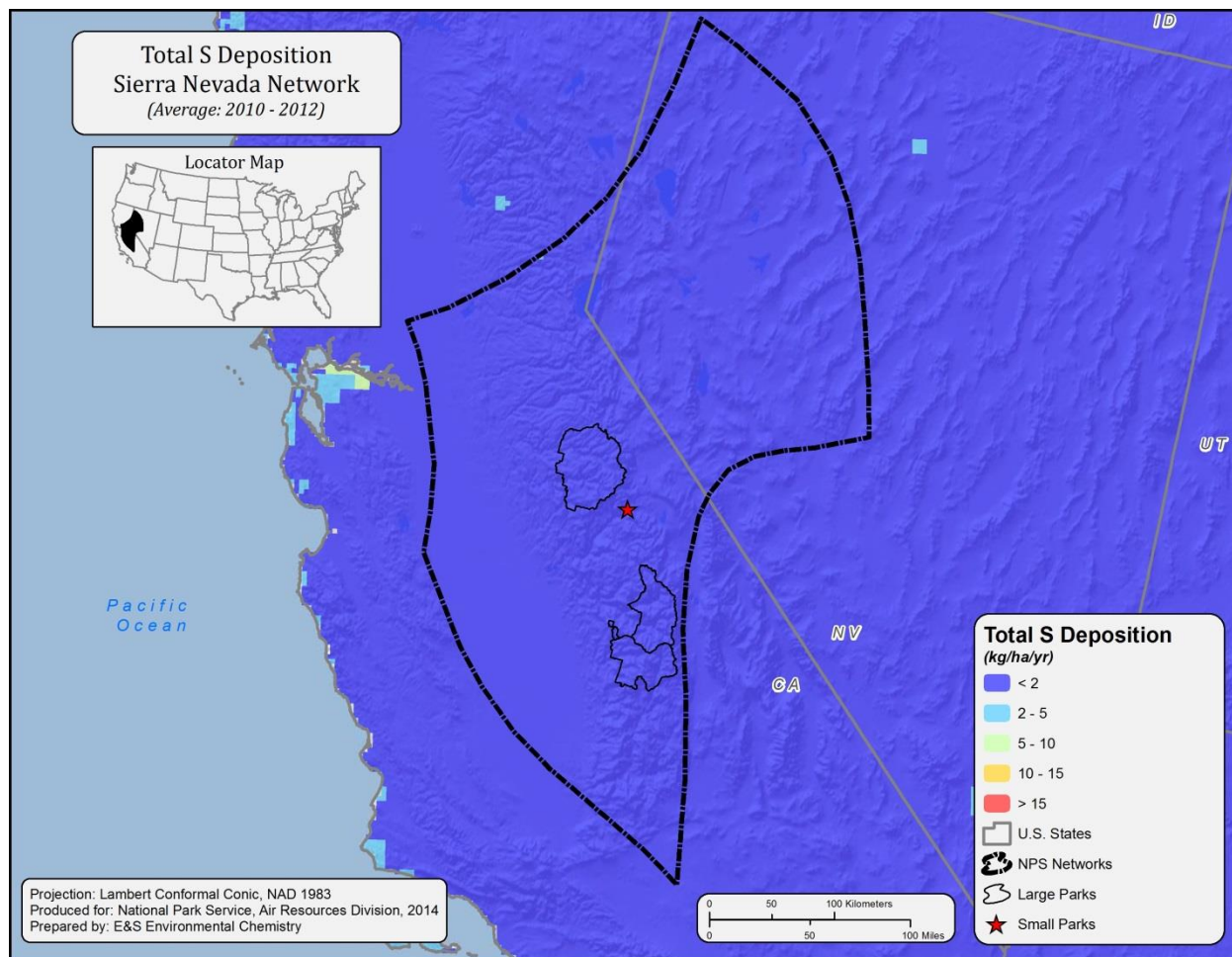
An atmospheric N budget for Sequoia NP calculated by Bytnerowicz et al. (2002) for the period July 7 to October 1, 1999 showed that reduced N compounds were more abundant than oxidized N compounds, suggesting that agricultural sources in the San Joaquin Valley were more important than industrial and transportation sources in the San Francisco Bay area to N air pollution in Sequoia NP. Ammonia constituted 34% of inorganic N, followed by NO₂ (30%), particulate NH₄⁺ (22%), and several less abundant oxidized N species.

Upwind emissions of pesticides can also constitute an important concern for parks in the SIEN. Pollutants can be emitted from source areas into the atmosphere as spray drift during pesticide application, via volatilization, and associated with wind-blown dust. Pesticides applied in California's Central Valley can be transported to sensitive high-elevation ecosystems in the nearby Sierra Nevada Mountains by prevailing west-to-east summer winds (Aston and Seiber 1997, Zabik and Seiber 1993).

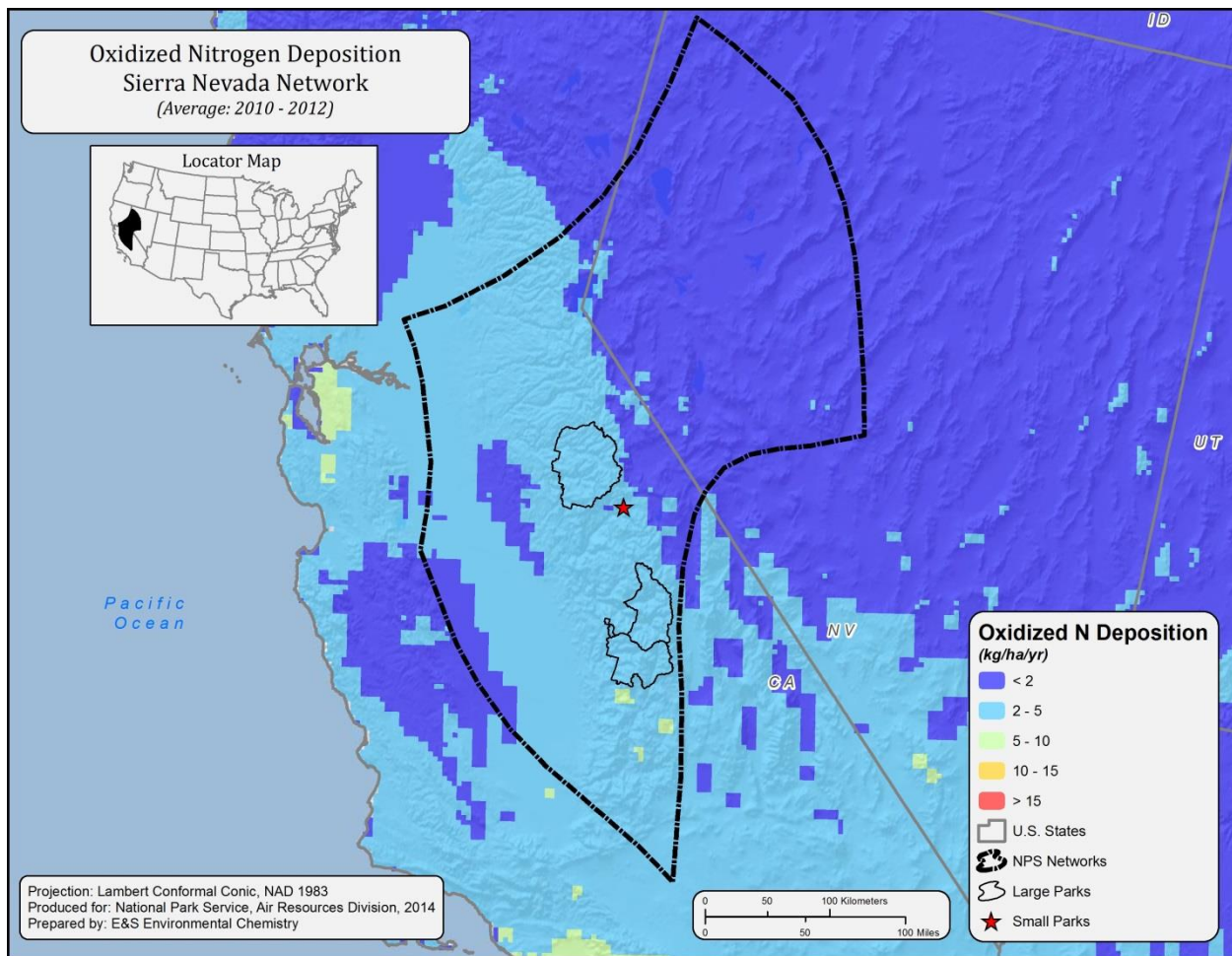
Snow accounts for most of the precipitation that falls at high elevation in the Sierra Nevada and therefore is an important factor influencing wet deposition of atmospheric contaminants. At Emerald Lake (2800 m) in SEKI, snow accounted for 88% of annual precipitation from 1983 to 2000 (Fenn et al. 2009, Sickman et al. 2001). Concentrations of N in snow in the Sierra Nevada can be an order of magnitude less than concentrations in rain (Fenn et al. 2009). National Atmospheric Deposition Program (NADP) wet deposition data illustrate increased NO₃⁻ and NH₄⁺ deposition from 1981 to 2001, although the increase was statistically significant only for NH₄ (0.037 kg N/ha/yr; $p \leq 0.01$; Fenn et al. 2003b). It is thought that NADP may have underestimated total wet deposition in these areas dominated by snow (Williams et al. 1998; http://snobear.colorado.edu/Markw/Research/williams_atmosenv_98.pdf)

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

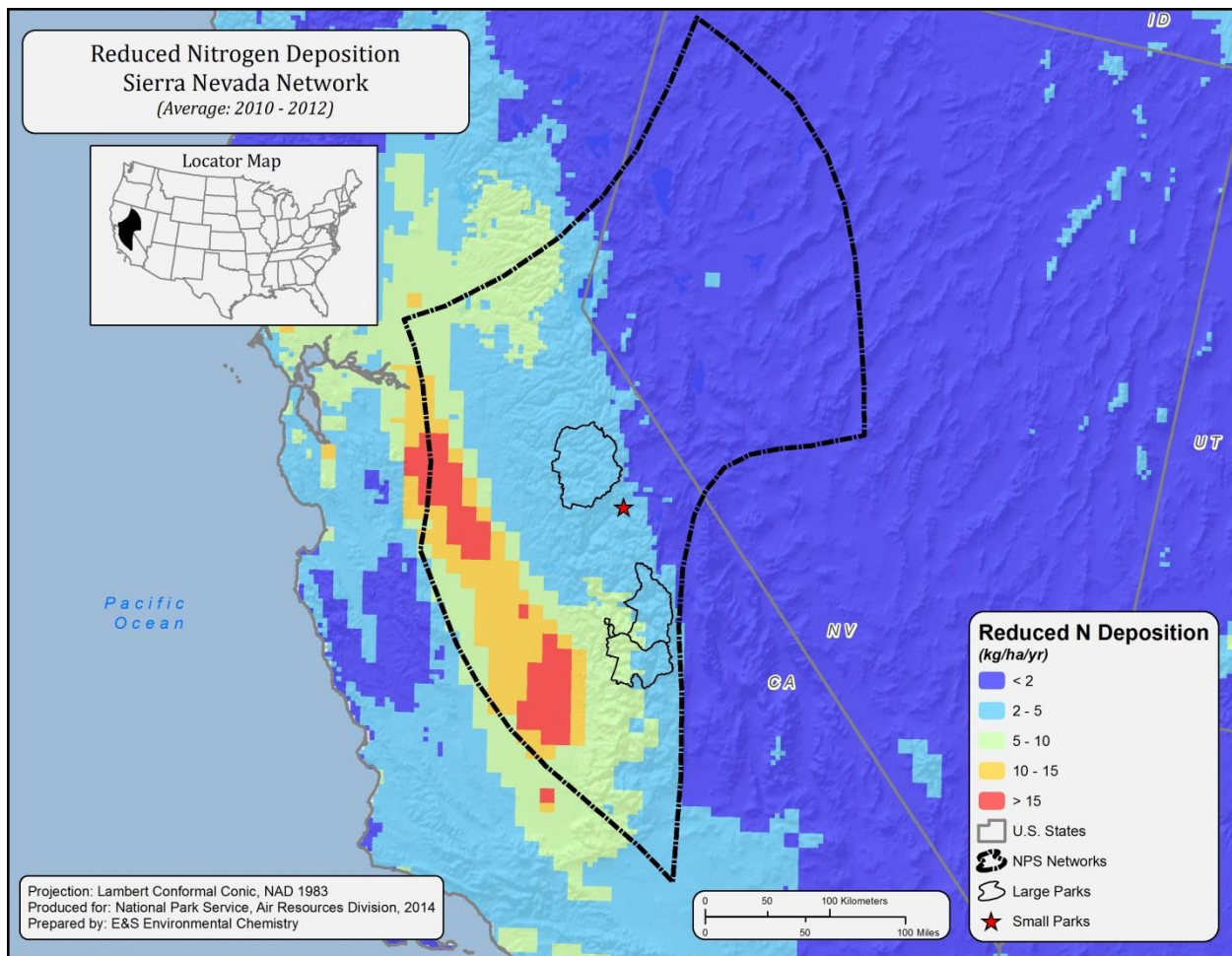
Park Code	Park Name	Parameter	2001 Average (kg/ha/yr)	2011 Average (kg/ha/yr)	Absolute Change (kg/ha/yr)	Percent Change	2011 Minimum (kg/ha/yr)	2011 Maximum (kg/ha/yr)	2011 Range (kg/ha/yr)
DEPO	Devils Postpile	Total S	0.89	1.10	0.21	24.2%	1.08	1.32	0.24
		Total N	3.56	4.92	1.36	38.2%	4.85	5.61	0.76
		Oxidized N	2.32	2.39	0.08	3.3%	2.36	2.63	0.27
		Reduced N	1.24	2.53	1.28	103.7%	2.49	2.98	0.50
KICA	Kings Canyon	Total S	1.31	1.55	0.24	19.3%	1.20	1.90	0.71
		Total N	5.75	7.21	1.46	25.2%	5.01	12.15	7.14
		Oxidized N	3.49	3.37	-0.13	-3.3%	2.45	4.39	1.94
		Reduced N	2.26	3.84	1.58	69.4%	2.34	7.80	5.46
SEQU	Sequoia	Total S	1.31	1.54	0.23	18.4%	1.06	1.90	0.84
		Total N	6.31	9.16	2.84	44.3%	5.91	13.27	7.37
		Oxidized N	3.71	3.72	0.01	0.4%	2.84	4.96	2.12
		Reduced N	2.60	5.43	2.83	106.7%	2.70	8.32	5.61
YOSE	Yosemite	Total S	1.11	1.30	0.18	16.5%	0.97	1.61	0.63
		Total N	4.40	5.76	1.36	31.0%	4.24	7.13	2.89
		Oxidized N	2.74	2.45	-0.29	-10.4%	2.03	2.93	0.90
		Reduced N	1.66	3.31	1.65	99.6%	2.20	4.20	1.99



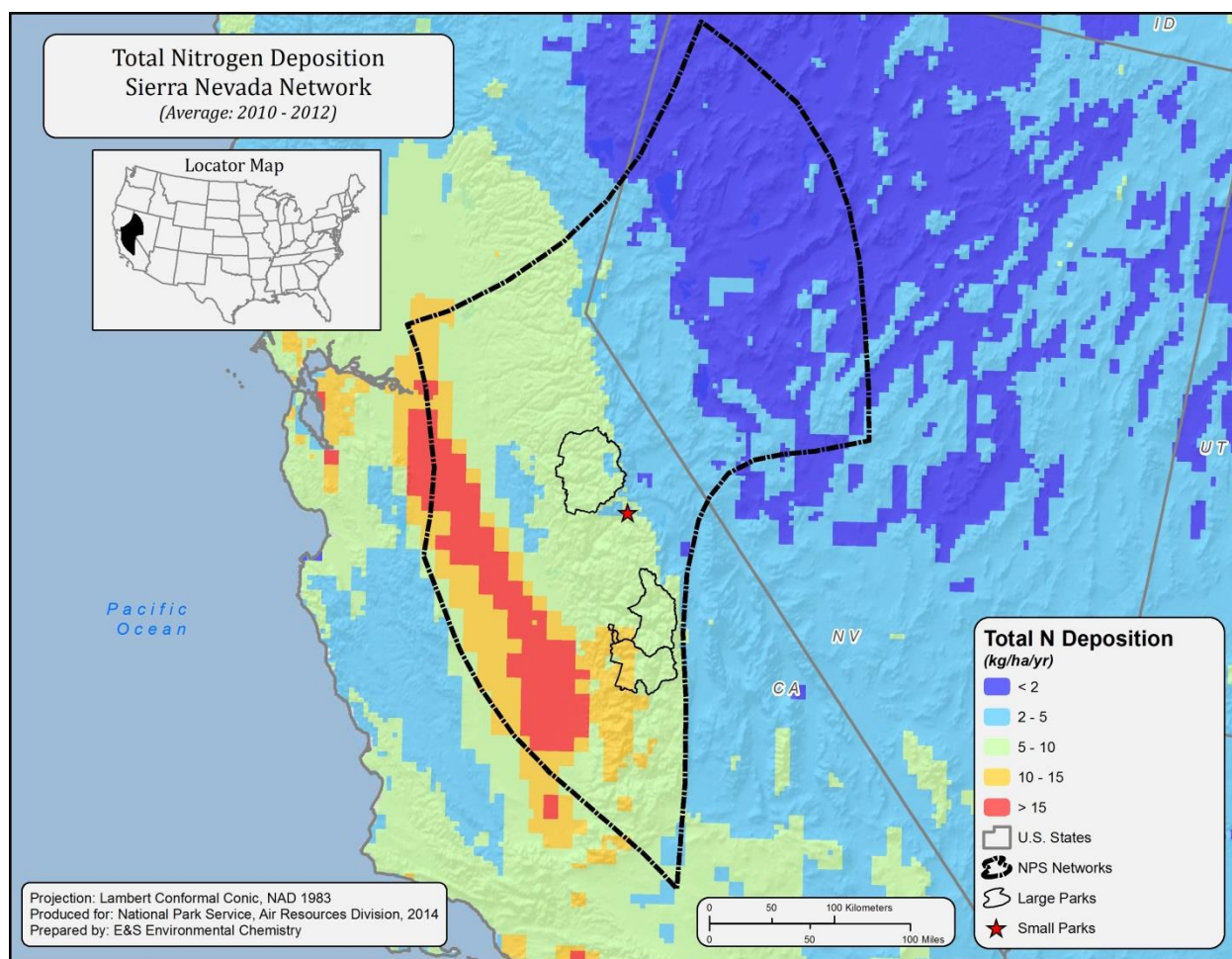
Map 5. Total S deposition estimated by TDEP for the three-year period centered on 2011 in and around the SIEN. (Source: Schwede and Lear 2014)



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



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



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

In the southern Sierra Nevada, winter storms are derived from relatively clean air masses that move onshore from Pacific frontal systems originating in the Gulf of Alaska. Non-winter precipitation is more commonly associated with localized thunderstorms that form from relatively N-enriched air from the Central Valley. As a consequence, N deposition exhibits seasonal variation, with lowest levels during winter (Fenn et al. 2003b).

McConnell et al. (1998) measured atmospheric inputs of current use pesticides (CUPs) to two locations (533 and 1,920 m elevation) in Sequoia NP by analyzing rain and snow samples. The highest pesticide concentration at both sites was for chlorothalonil; other quantitatively important organic chemicals in the wet deposition included malathion, diazinon, and chlorpyrifos.

Both SO₂ emissions and atmospheric sulfate (SO₄²⁻) concentrations at Interagency Monitoring of Protected Visual Environments (IMPROVE) visibility monitoring sites decreased during the 1990s throughout much of the western United States (Malm et al. 2002). Decreases in S emissions were largest in California (-37%). This may have contributed to visibility improvement.

Some research has been conducted on cloud deposition of S and N in the SIEN region. Collett et al. (1990) selected two sites in the Sierra Nevada to serve as locations for monitoring the chemical composition of cloud water. The sites were at Lower Kaweah (1,856 m) in Sequoia NP and at Turtleback Dome (1,590 m) in YOSE. Both sites were located in open areas which easily intercept approaching clouds. Cloudwater interception was recorded between September 1987 and August 1988. The two peak months for cloudwater interception were November and April.. The pH of the cloudwater samples collected in Sequoia NP ranged from 3.9 to 6.5, with fall samples tending to be somewhat more acidic than those collected during the winter or spring. The inorganic composition of the cloudwater was dominated by NO_3^- , SO_4^{2-} , and NH_4^+ . Cloudwater samples at Turtleback Dome tended to be more acidic than those collected at Lower Kaweah during the spring of 1988. In Sequoia NP, in particular, the neutralization of cloudwater acidity by NH_3 was largely responsible for maintaining the pH of cloudwater above levels commonly seen at sites in the eastern United States.

Collett et al. (1989) had previously suggested that the deposition of NO_3^- , SO_4^{2-} , and NH_4^+ by cloudwater interception at Lower Kaweah might be comparable to amounts contributed by precipitation. However, based on the data that were collected by Collett et al. (1990), estimates of total deposition from cloudwater interception appear to be much lower than previously predicted, especially for SO_4^{2-} . Revised cloudwater deposition estimates were still significant compared to precipitation inputs, and the estimated cloudwater deposition inputs of NH_4^+ and NO_3^- at this site were greater than 50% of the respective wet deposition inputs.

Acidification

Sullivan et al. (2011b) evaluated relative risk of acidification for all I&M networks nationwide. The network rankings developed by Sullivan et al. (2011b) for acid Pollutant Exposure, Ecosystem Sensitivity to acidification, and Park Protection yielded an overall network acidification Summary Risk ranking for the SIEN that was among the highest of all 32 I&M networks. The overall level of concern for acidification effects on SIEN parks was judged by Sullivan et al. (2011b) to be Very High.

The SIEN parks were ranked low (DEPO, SEKI) or Moderate (YOSE) by Sullivan et al. (2011b) in acid Pollutant Exposure (Table 2). However, Ecosystem Sensitivity to acidification for all three of the larger parks was ranked in the highest quintile (Very High; Table 2). All three contain numerous high-elevation lakes and streams, low-order streams, and steep terrain; in addition, all three occur within regions of known acid-sensitivity. DEPO was ranked in the second highest quintile for Ecosystem Sensitivity to acidification (High; Table 2). While rankings are an indication of risk, park-specific data, particularly data on ecosystem sensitivity, are needed to fully evaluate risk from acidification.

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
Devils Postpile	DEPO	Low	High
<i>Kings Canyon</i>	KICA	Low	Very High
<i>Sequoia</i>	SEQU	Low	Very High
<i>Yosemite</i>	YOSE	Moderate	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 mi².

Ecosystem Sensitivity to acidification rankings take into account land slope, elevation, and stream order, which often influence the degree of acid neutralization provided by soils and bedrock within the watershed. Most of the land in SEKI is very steep, in the range of 40° to 50°. Lands within YOSE are also generally steep; most stream basins have slopes of 30° to 40°, with some 10 digit hydrologic unit codes (HUCs) averaging 40° to 50° slope. These steep slopes suggest an increased potential for acid sensitivity of aquatic ecosystems.

Acidification of Terrestrial Ecosystems

Portions of the mountainous West contain large areas of exposed bedrock, with little soil or vegetative cover to neutralize acidic inputs. This is particularly true of alpine regions of the Sierra Nevada (Charles 1991). It is likely that alpine terrestrial ecosystems in the SIEN are highly sensitive to acidification. In view of the relatively low levels of acidic deposition, however, effects to date are expected to have been minimal.

Data on the possible effects of S and N deposition on the acid-base characteristics of coniferous forest ecosystems in the SIEN region are spotty and inconclusive. What data are available suggest that California mixed coniferous forests may be less susceptible to N deposition stress than coniferous forests in the eastern United States. For example, a study by Bytnerowicz (2002) demonstrated increased bole growth in ponderosa pine and black oak with additions of 50 kg N/ha/yr. However, a study by Temple (1992) found that ponderosa pine seedlings exposed to acidic precipitation (pH 5.3, 4.4 and 3.5) showed no significant changes in growth. Fenn et al. (2003a) reported that deposition levels of 20 to 35 kg N/ha/yr contributed to increased NO_3^- leaching and soil acidity and decreased base saturation in southern California ecosystems, but they did not report quantitative measures of plant growth. Most coniferous forests in the SIEN receive much lower levels of atmospheric N deposition and are unlikely to be measurably impacted by acidification.

Acidification of Aquatic Ecosystems

The Cascade and Sierra Nevada Mountains (including within the SIEN region) constitute the mountain ranges with the greatest number of acid-sensitive aquatic resources in the country (Landers et al. 1987). Surface waters in these regions are among the most poorly buffered in the United States (Landers et al. 1987, Melack and Stoddard 1991). Lakes in the Sierra Nevada are especially sensitive to impacts from acidic deposition because of the predominance of granitic bedrock, thin acidic soils, large amounts of precipitation, sparse coniferous vegetation, and dilute nature of the lakes (McColl 1981, Melack et al. 1985, Melack and Stoddard 1991). The hydrologic cycle is dominated by the annual accumulation and melting of a dilute, mildly acidic (pH 5.5) snowpack (Melack et al. 1997). The acid-base chemistry of lake (and presumably also stream) waters in the SIEN region appears to be primarily a function of the interactions among several key parameters and associated processes: atmospheric deposition, bedrock geology, the depth and composition of surficial deposits and associated hydrologic flowpaths, and the occurrence of soils, tundra, and forest vegetation (Sullivan 2000).

Because of the proximity of western urban and industrial pollution sources to individual mountain ranges, it is important to consider emissions in the immediate vicinity of sensitive resources as well as regional emissions (Sullivan and Eilers 1994). Atmospheric deposition in the far western ranges, including the Sierra Nevada, is largely influenced by local emissions, particularly emission sources to the west (upwind) of sensitive resources.

The weight of evidence suggests many high-elevation lakes in SIEN parks receive N deposition sufficiently high to cause limited chronic NO_3^- leaching. It does not appear that widespread chronic lake or stream acidification has occurred to any significant degree, although some episodic acidification has likely occurred (Sullivan 2000). It is important to note that even low to moderate concentrations of NO_3^- in surface waters within SIEN parks might be significant in view of: (1) the low base cation concentrations in many surface waters; (2) potential for continuing N deposition to eventually exhaust natural assimilative capabilities; and (3) the fact that these observations are typically based on summer or fall data. Acid anion concentrations in most western mountain lakes are low during summer and fall, but can be higher during spring snowmelt, mostly in the form of pulses during snowmelt (Melack et al. 1989). There is good evidence that high elevation lakes are

recovering from a 20th century nutrient enrichment episode that likely changed lake chemistry (Sickman et al. 2003).

A large number of water quality studies have been conducted within the parks in the SIEN, and several were summarized by Sullivan et al. (2001). Water samples were collected by helicopter from 170 lakes in SEKI and YOSE in September 1965. pH values ranged from 4.7 to 7.3, with an arithmetic mean and median both equal to pH 6.0. Specific conductance measurements ranged from 2.4 to 110 $\mu\text{S}/\text{cm}$, with an arithmetic mean of 8.0 and a median of 7.0 (Bradford et al. 1968, Clow et al. 2003). These low values of specific conductance reflect low ionic strength and suggest that sensitivity of some lakes to acidification may be high. A follow-up study was conducted by randomly sampling 124 lakes in the three parks in July 1980, 1981, 1982, and 1983 during the spring thaw, and also in October 1980 before the winter freeze (Bradford et al. 1983). The results suggested that lake water acidity, total electrolyte concentration, and the concentrations of a number of trace elements did not increase between 1965 and 1983. Median values for lakewater SO_4^{2-} in July 1980, October 1980, and July 1981 were 8.3, 8.8, and 11.0 $\mu\text{eq}/\text{L}$, respectively. Similarly, the median concentrations of lakewater NO_3^- were 7.1, 2.9, and 5.7 $\mu\text{eq}/\text{L}$, respectively. Bradford et al. (1983) also sampled feeder streams and snow. These samples were analyzed for pH, conductivity, and bicarbonate concentration. Median pH value of the feeder streams was equal to that of the lakewater (6.4). In contrast, snowmelt water had a median pH of 5.6.

The National Acid Precipitation Assessment Program (NAPAP) State of Science and Technology Reports and the Integrated Assessment (NAPAP 1991) provided only a cursory treatment of aquatic effects issues in the SIEN region, largely because it was well known that atmospheric deposition of S and N were generally low compared to areas in the East (Sullivan 2000). The available information on acid-base chemistry of surface waters in the SIEN region is based on synoptic data from EPA's Western Lakes Survey (WLS; Landers et al. 1987) and some more localized studies (cf., Shaw et al. 2014). The WLS sampled 11 lakes in Kings Canyon NP and 9 lakes in Sequoia NP, plus an additional 14 lakes within 16 miles (25 km) of SEKI (Sullivan et al. 2001). Nitrate concentrations were virtually undetectable in most western lakes sampled by the WLS in the fall (Landers et al. 1987). However, in a few cases, fall NO_3^- concentrations were surprisingly high. For example, in the Sierra Nevada about 10% of the WLS lakes had NO_3^- concentrations above 5 $\mu\text{eq}/\text{L}$ (Sullivan and Eilers 1994).

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 for acidity of surface waters based on multiple approaches for estimating base cation weathering; modified F-factor, regional regression model, and MAGIC model. 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; NPS Vital Signs program; and 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. The CLAD database included 11 sites in Kings Canyon NP and 12 sites in each of Sequoia NP and YOSE. All three parks

had some modeled estimates of CL = 0 eq S/ha/yr, suggesting substantial acid sensitivity of surface waters in these parks.

Shaw et al. (2014) used the Steady State Water Chemistry (SSWC) model to estimate the steady-state CL of acidity for 208 lakes in the Sierra Nevada. Study lakes were generally dilute (mean specific conductance 8 $\mu\text{S}/\text{cm}$), with low ANC (mean 57 $\mu\text{eq}/\text{L}$). Most were located in Forest Service wilderness areas, some in proximity to SIEN parks. Using a critical ANC limit of 10 $\mu\text{eq}/\text{L}$ to protect aquatic biota from effects of water acidification, the SSWC model predicted a CL of 149 eq/ha (14.9 meq/m^2) of acidity for watersheds on granitic bedrock. More than one third of the lakes received acidic deposition in exceedance of the CL. The median study lake showed a CL exceedance of about 80 eq/ha (8 meq/m^2). Based on these calculations, Shaw et al. (2014) concluded that high elevation lakes in the Sierra Nevada have not fully recovered from the effects of acidic deposition despite large improvements in air quality over the last several decades.

Sequoia and Kings Canyon National Parks

The potential for chronic, and especially episodic, acidification of lakes and streams in SEKI from N and S deposition is an important water quality concern. This concern is based largely on the moderate levels of N deposition that occur in the parks, extreme sensitivity to acidification of many high-elevation surface waters, potential short-term effects of acidic rain- on-snow events during the snowmelt period, and documented importance of episodic hydrological processes in alpine and subalpine watersheds within the parks. Significant effort has been expended to determine the extent to which acidic deposition may have contributed to chronic and/or episodic acidification in these parks and the extent of acidification that would be required to elicit adverse biological impacts. The results of these studies paint a rather complete picture of the acid-base status of freshwater resources in SEKI. These results are also relevant to YOSE.

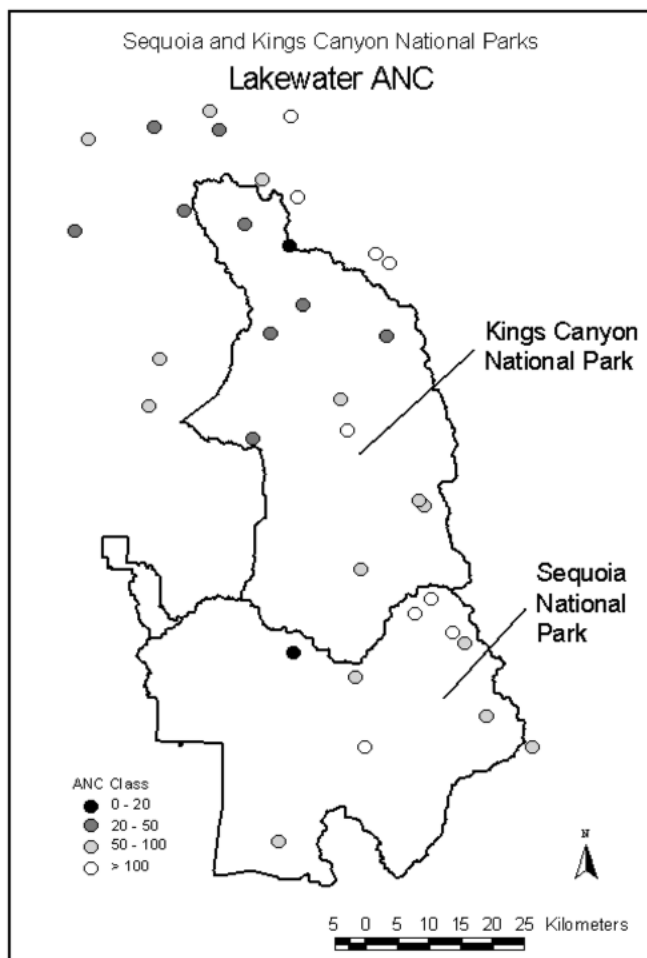
About one third of the lakes sampled by the WLS in and near SEKI had acid neutralizing capacity (ANC) < 50 $\mu\text{eq}/\text{L}$, and two of the lakes in the park had ANC < 20 $\mu\text{eq}/\text{L}$ (Map 9). These lakes, especially those having ANC < 20 $\mu\text{eq}/\text{L}$, are sensitive to potential acidification from acidic deposition. All of the most sensitive lakes had pH between 6.1 and 7.0, and most had sum of base cation concentrations between about 25 and 50 $\mu\text{eq}/\text{L}$. Most were small (< about 7 ha), occurred in watersheds less than about 100 ha in area, and were situated at elevations ranging from about 2,800 m to 3,700 m.

A chemical survey of 101 high-altitude lakes in 7 national parks in the western United States was conducted by the U.S. Geological Survey (USGS) during the fall of 1999 (Clow and Sueker 2000); 72 of the lakes were previously sampled during the fall of 1985 as part of the WLS. This study sampled 24 lakes in SEKI, including all of the previously sampled WLS lakes. Five lakes had ANC < 30 $\mu\text{eq}/\text{L}$, with the lowest being 7 $\mu\text{eq}/\text{L}$. That same lake (4A1-056) was the only one having relatively high NO_3^- concentration (9 $\mu\text{eq}/\text{L}$). Eleven lakes had ANC < 50 $\mu\text{eq}/\text{L}$. Of the 10 lakes sampled in YOSE, 9 of which had been included in the WLS, all had ANC $\leq$ 75 $\mu\text{eq}/\text{L}$ and 4 had

ANC $\leq$ 30 $\mu\text{eq/L}$. Only one lake in YOSE exhibited NO_3^- concentration higher than 0.1 $\mu\text{eq/L}$ (Clow and Sueker 2000).

In general, lake SO_4^{2-} concentrations in the SIEN region decreased between 1985 and 1999, in response to regional decreases in SO_2 emissions and S deposition (Clow et al. 2003). In addition, lake NO_3^- concentrations were slightly lower in 1999, probably at least in part because rain prior to the 1985 survey may have caused elevated NO_3^- concentration in some lakes at the time of sampling (Clow et al. 2003). This finding reinforced the idea that changes in precipitation should be included in an assessment of water chemistry trends (cf., Bayley et al. 1992, Webster and Brezonik 1995). Lake ANC was relatively consistent between the two surveys, although it decreased to some extent in SEKI in response to a general decrease in solute concentrations which might have been caused partly by climatic differences between the two sampling periods (Clow et al. 2003).

The concentrations of SO_4^{2-} in the most acid-sensitive lakes sampled by Clow and Sueker (2000) tended to be relatively low; lakewater SO_4^{2-} concentration ranged between about 3 and 10 $\mu\text{eq/L}$ in most cases. Such concentrations are approximately what would be expected, assuming average SO_4^{2-} concentrations in precipitation of about 3 to 5 $\mu\text{eq/L}$, negligible dry deposition, and less than 50% evapotranspiration (Sullivan et al. 2001). Although concentrations of SO_4^{2-} in lakes in the SIEN region are generally low, at some locations geologic sources contribute substantial amounts of SO_4^{2-} to lakewaters (Sullivan et al. 2001). Clow et al. (1996) presented a comparison of median major ion chemistry from four surface water surveys in the Sierra Nevada (Table 3). Water chemistry measured in the various surveys was similar, but granitic watersheds were more acid-sensitive than non-granitic watersheds, and were less likely to exhibit high SO_4^{2-} concentrations suggestive of watershed sources of S. Many of the WLS lakes in SEKI, including two of those having low ANC ($< 50 \mu\text{eq/L}$), had relatively high concentrations of SO_4^{2-} ($>> 10 \mu\text{eq/L}$), which were likely the result of watershed sources of S. Nitrate concentrations were variable in the acid-sensitive lakes, ranging from near zero to 10 $\mu\text{eq/L}$. During the 1980s, an Integrated Watershed Study (IWS) was conducted at seven lakes in the Sierra Nevada, including Emerald Lake and surrounding watersheds in Sequoia NP ($\sim 3,000$ m elevation) to determine the effects of acidification on surface waters (Tonnessen 1991). The volume-weighted mean lake outlet pH of the seven study lakes was 6.05, and ranged from 5.6 to 6.7 (Melack et al. 1998). Three lakes (Lost, Pear, and Emerald) had volume-weighted mean ANC in the range of 15 to 30 $\mu\text{eq/L}$ and were classified by Melack et al. (1998) as low in ANC. Moderate ANC waters (Topaz, Spuller, and Marble Fork) exhibited mean ANC in the range of 30 to 50 $\mu\text{eq/L}$. Crystal and Ruby Lakes had mean annual ANC $> 50 \mu\text{eq/L}$.



Map 9. Lakewater ANC in and around SEKI, based on results of the Western Lakes Survey.

Table 3. Comparison of major ion chemistry data from four surface water synoptic surveys in the Sierra Nevada. Median values (first and third quartiles in parentheses) given in $\mu\text{eq/L}$, except SiO_2 in $\mu\text{mol/L}$. (Source: Clow et al. 1996)

	Elevation (m)	pH	Ca^{2+}	Mg^{2+}	Na^+	K^+	Cl^-	NO_3^-	SO_4^{2-}	HCO_3^-	SiO_2
Clow et al. (1996), ($n = 27$)	2164	6.8 (6.7-7.0)	39 (34-83)	7 (5-12)	28 (22-59)	4.2 (4-6)	6 (5-18)	2.1 (0.0-3.9)	10 (7-12)	42 (36-64)	56 (39-84)
Melack et al. (1985), granitic ($n = 44$)	3389	6.9 (6.4-7.2)	37 (22-54)	5 (3-7)	16 (10-24)	6 (4-15)	8 (5-16)	0.4 (0.1-2.4)	13 (9-20)	44 (25-65)	
Melack et al. (1985), non-granitic ($n = 29$)	3121	7.2 (7.0-7.8)	70 (34-308)	10 (5-25)	26 (18-48)	12 (7-20)	12 (8-21)	0.2 (0.1-0.9)	31 (18-91)	71 (41-258)	
WLS (population) ($N = 2119$)	3008	6.9 (6.6-7.3)	43 (29-104)	6 (3-9)	19 (11-21)	4	2 (1-3)	0.4 (0.1-1.7)	7 (4-7)	60 (37-130)	33 (22-60)

Paleolimnological reconstructions of lakewater pH and ANC were calculated by Holmes et al. (1989) at 24 depth intervals at Emerald Lake in Sequoia NP for the period 1825 to the present. Significant trends were not found for either pH or ANC, and the authors concluded that Emerald Lake had not acidified in response to acidic deposition. Whiting et al. (1989) completed paleolimnological analyses of three additional lakes in the Sierra Nevada. Eastern Brook Lake (pH = 7.06) showed evidence of both long-term alkalization (~ 0.3 pH units over the past 200 years) and pH fluctuations since 1970. Lake 45 (pH = 5.16) may have acidified slightly (~ 0.2 pH units) over the previous 60 years. Lake Harriet (pH = 6.52) showed no significant change.

Williams and Melack (1989) examined variation in the onset of snowmelt in portions of the Emerald Lake watershed and effects on the magnitude and timing of ionic pulses in the various sub-basins. Source areas of snowmelt runoff varied spatially and temporally in response to slope and aspect. Concentrations of NO_3^- and SO_4^{2-} in streams were correlated with the amount of snowmelt in each sub-basin. Inflows to Emerald Lake had elevated concentrations of NO_3^- (~18 $\mu\text{eq/L}$) and SO_4^{2-} (~9 $\mu\text{eq/L}$) at initiation of snowmelt, which then decreased as snowmelt progressed. The onset of snowmelt, and accompanying ionic pulses in streamwater, shifted from sub-basins with southwesterly aspect to those with northerly aspect (Williams and Melack 1989).

Thirty lakes were selected at random for study by Jenkins et al. (1994) from the subset of Sierra Nevada lakes above approximately 2,400 m elevation. The lakes were selected using EPA's Environmental Monitoring and Assessment Program (EMAP) area-based sampling technique which allowed extrapolations to be performed to a population of 1,404 lakes that are larger than 1 ha in surface area. The lakes were sampled for their water chemistry and to assess populations of fish and macroinvertebrates that were present in the lakes and their associated streams. The results of water chemistry analyses were generally similar to those found in the WLS, although lakes in the survey of Jenkins et al. (1994) were higher in elevation and smaller in surface area overall as compared with the WLS lakes. Median pH and ANC values were slightly lower than the medians reported in the WLS, and NO_3^- concentrations were higher. Several lakes at the southeastern border of Kings Canyon NP were acidic from watershed sources of S. These lakes had high SO_4^{2-} and aluminum (Al) concentrations. In the lakes represented by the study, 8% had pH less than 6.

Yosemite National Park

High-elevation lakes and streams in YOSE are extremely sensitive to acidification from even moderate levels of S or N deposition. There are about 268 lakes and 92 rivers and streams (1,415 km in length) within YOSE. Geological factors, including jointing of the bedrock and the distribution of glacial till, appear to exert strong controls on water chemistry (Clow et al. 1996).

Water chemistry data from three surface water surveys in the upper Merced River watershed conducted in August 1981, June 1988, and August 1991 were analyzed and compared by Clow et al. (1996) with mapped geological, hydrological, and topographic features to try to identify solute sources and major processes that control water chemistry during base flow periods. A total of 23 sites were sampled during the three surveys. The water at most of the sample sites was dilute, with ANC values ranging from 26 to 77 $\mu\text{eq/L}$ at most sites. The ANC was considerably higher in two of the sampled subwatersheds, however, ranging from 51 to 302 $\mu\text{eq/L}$. Concentrations of weathering

products in surface water were correlated with the fraction of each subwatershed that was underlain by surficial material, primarily glacial till.

The WLS sampled 9 lakes within YOSE and an additional 14 lakes within 25 km of YOSE. Two-thirds of the WLS lakes in YOSE, and nearly half of those near the park, had ANC < 50 $\mu\text{eq/L}$. Three of the sampled lakes in and near the park had ANC < 20 $\mu\text{eq/L}$. Many of the sensitive low-ANC lakes were small (< 10 ha), as is typically the case for acid-sensitive Sierra Nevada lakes, although several were considerably larger (16 to 30 ha). The pH values in the sensitive lakes were generally between 6.2 and 7.0, although one lake outside the park had pH < 6. Lakewater SO_4^{2-} concentrations were generally between about 3 and 12 $\mu\text{eq/L}$ in the sensitive lakes. There were also three lakes within YOSE with slightly higher SO_4^{2-} concentration (14 and 18 $\mu\text{eq/L}$), which could be partly attributable to watershed sources of S, and one lake outside the park with very high SO_4^{2-} (92 $\mu\text{eq/L}$) which is almost certainly attributable to geologic S. The three lakes having higher-than-expected SO_4^{2-} concentration were not among the most acid-sensitive of the sampled lakes (ANC = 71, 57, 38 $\mu\text{eq/L}$, respectively). Although most of the sampled lakes had very low NO_3^- concentration (< 2 $\mu\text{eq/L}$), there was one lake in YOSE with relatively high NO_3^- (8 $\mu\text{eq/L}$), and two lakes outside the park with similarly high NO_3^- (6 and 10 $\mu\text{eq/L}$). All of the lakes having high NO_3^- were low in ANC (27 to 38 $\mu\text{eq/L}$) and were over 3,100 m elevation. The most acid-sensitive lakes in and near YOSE, i.e., those having ANC less than about 30 $\mu\text{eq/L}$, had very low concentrations of base cations (about 20 to 35 $\mu\text{eq/L}$), about half of which was calcium (Ca^{2+}), and low dissolved organic carbon (DOC; < 2 mg/L). All are presumably highly-sensitive to chronic, and especially episodic, acidification if S or N deposition increases substantially in the future.

Surface waters in YOSE generally consist of chains of relatively small lakes connected by high-gradient streams (Clow et al. 2002, Clow et al. 2003). Clow et al. (2010) sampled the water chemistry of 21 streams and the outlets of 31 small (typically < 10 ha) lakes in YOSE during September, 2003. Samples were collected during baseflow conditions at the end of the growing season, and therefore generally represented NO_3^- concentration annual minima and ANC maxima. Surface water NO_3^- concentrations ranged from < 1 to 14 $\mu\text{eq/L}$, and were highest in small, high-elevation watersheds on the eastern side of the park. Surface water ANC values were low at sites located at high elevation and increased in a downstream direction. The minimum measured ANC was 11 $\mu\text{eq/L}$.

Clow et al. (2010) used multiple linear regression (MLR) to estimate fall NO_3^- concentration and ANC in surface waters across YOSE. The MLR models explained 84% of the variation in NO_3^- and 70% of the variation in ANC. Surface water NO_3^- concentration was positively associated with elevation, abundance of neoglacial till and talus deposits, and amount of unvegetated terrain; and negatively correlated with amount of alluvium and riparian areas. The positive association with elevation reflects cold temperature and short growing season which limit N uptake by vegetation and aquatic biota at high elevation. Unglaciaded areas and areas of neoglacial till and talus would be expected to lack well-developed soil and exhibit limited N assimilation. Nitrate concentrations were also negatively associated with the percent of mixed conifer forest in the watershed in response to high N uptake in such forests (Sickman et al. 2002). Winter N deposition was not correlated with

surface water NO_3^- concentration. Thus, watershed features seemed to exert greater control on surface water NO_3^- concentration than N input rate. Surface water ANC was positively correlated with watershed area and abundance of metamorphic rocks, and negatively correlated with the amount of unvegetated terrain, water, and N deposition in the watershed. The positive relationship between surface water ANC and watershed area reflected the influence of water residence time and water/rock interactions. Similarly, areas of alluvium and Pleistocene till would be expected to have deeper, better-developed soils allowing greater interaction with drainage water (Clow et al. 2010). ANC was positively correlated with forest cover due to weathering in forest soil and negatively correlated with winter N and S deposition and snow duration, reflecting the influence of deposition and snow dynamics.

In YOSE, talus and unvegetated terrain are most common at high elevation. Clow et al. (2010) grouped the major geological materials into four classes, ranging from high to low sensitivity to acidic deposition: 1) neoglacial and talus; 2) felsic intrusive rocks such as granite, granodiorite, and diorite; 3) mafic intrusive rocks; and 4) metamorphic rocks, alluvium and Pleistocene glacial till. On the basis of this geologic classification, most surface waters in YOSE are highly sensitive to acidic deposition (Map 10), consistent with their known low ionic strength (Clow et al. 2002). There are also scattered areas of low sensitivity throughout the park. Many are associated with alluvium and Pleistocene glacial till (Map 10). There are metamorphic rock outcrops near the Sierran Crest north of Tioga Pass that contain carbonate and sulfide minerals. In this area, ANC tends to be high, along with Ca^{2+} and SO_4^{2-} . Many waters in this area have SO_4^{2-} concentration $> 30 \mu\text{eq/L}$, much of which is derived from mineral weathering rather than atmospheric deposition. The MLR equations were applied by Clow et al. (2010) to 1407 stream reaches in YOSE, and the predicted patterns in surface water NO_3^- concentration and ANC were mapped (Map 11).

Temporal Variability in Water Chemistry

Decreases in pH with increases in flow are nearly ubiquitous in drainage waters throughout acid-sensitive portions of the United States (Wigington et al. 1990). During episodes, which are driven by rainstorms and/or snowmelt events, both discharge (streamflow volume per unit time) and water chemistry change, sometimes dramatically. Episodes in the SIEN region are generally accompanied by changes in at least two or more of the following chemical parameters: ANC, pH, base cations, SO_4^{2-} , NO_3^- , Al organic acid anions, and DOC (Sullivan 2000). Chemical changes during 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 (at near-coastal locations) the neutral salt effect. Episodic acidification pulses may last for hours to weeks, and sometimes result in depletion of ANC in acid-sensitive streams and lakes to negative values.

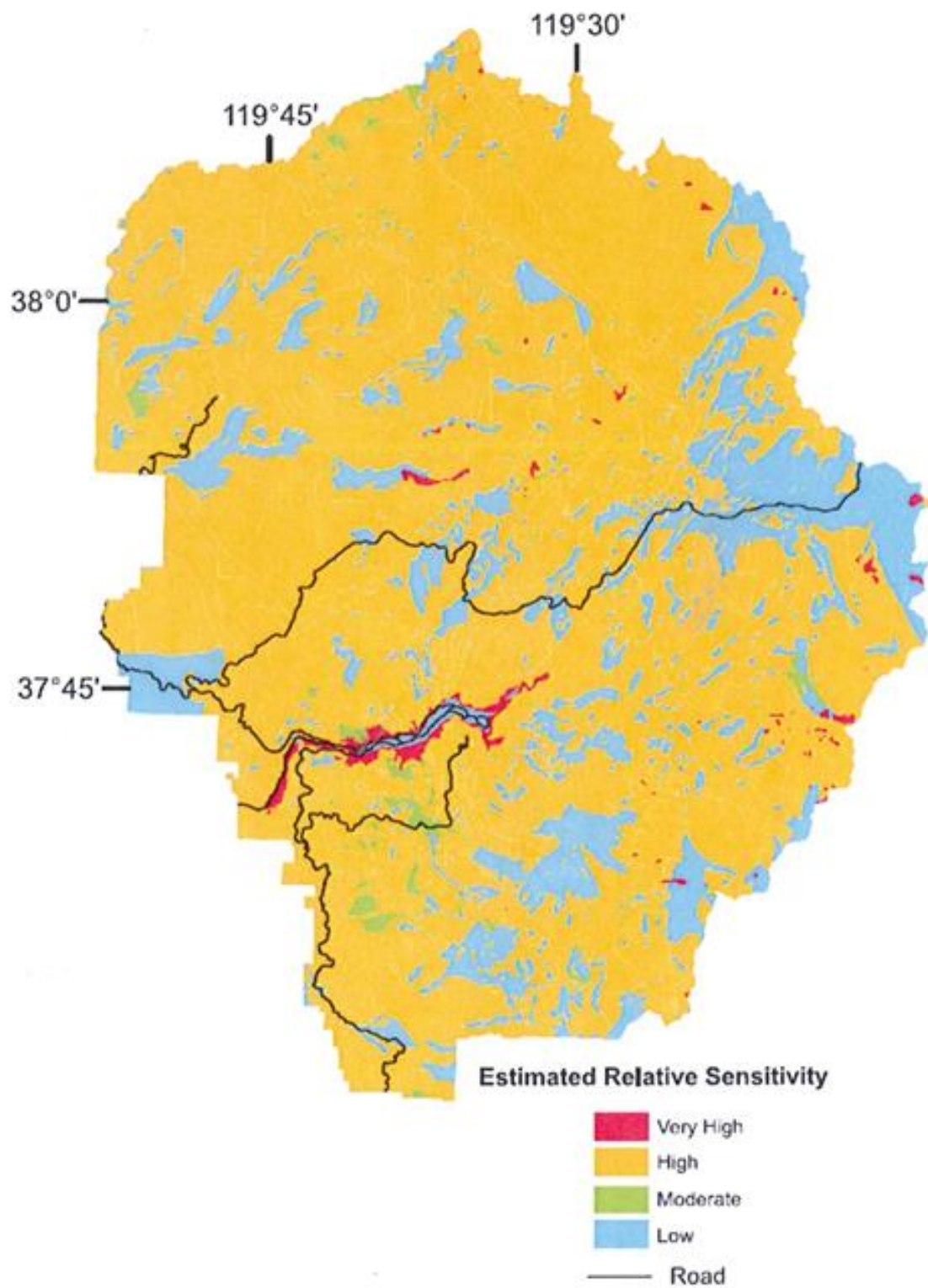
The most important factor governing watershed sensitivity to episodic acidification is the pathway followed by snowmelt and stormflow water through the watershed. These pathways determine the extent of acid neutralization provided by the soils and bedrock in that watershed. During high flows caused by snowmelt or rainfall events, flow-routing favors water flowpaths through upper soil horizons. During such events, drainage water chemistry typically reflects the lower pH, higher

organic content, and lower ANC of upper soil horizons (Sullivan 2000). Storm flow and snowmelt are often associated with episodes of surface water acidity due to an increase in the proportion of flow derived from water that has moved laterally across exposed rock or through the surface soil without infiltration to deeper soil horizons (Wigington et al. 1990). High-elevation watersheds with steep topography, extensive areas of exposed bedrock, deep snowpack accumulation, and shallow, base-poor soils tend to be most sensitive to episodic acidification. Such features are common in park lands within the SIEN.

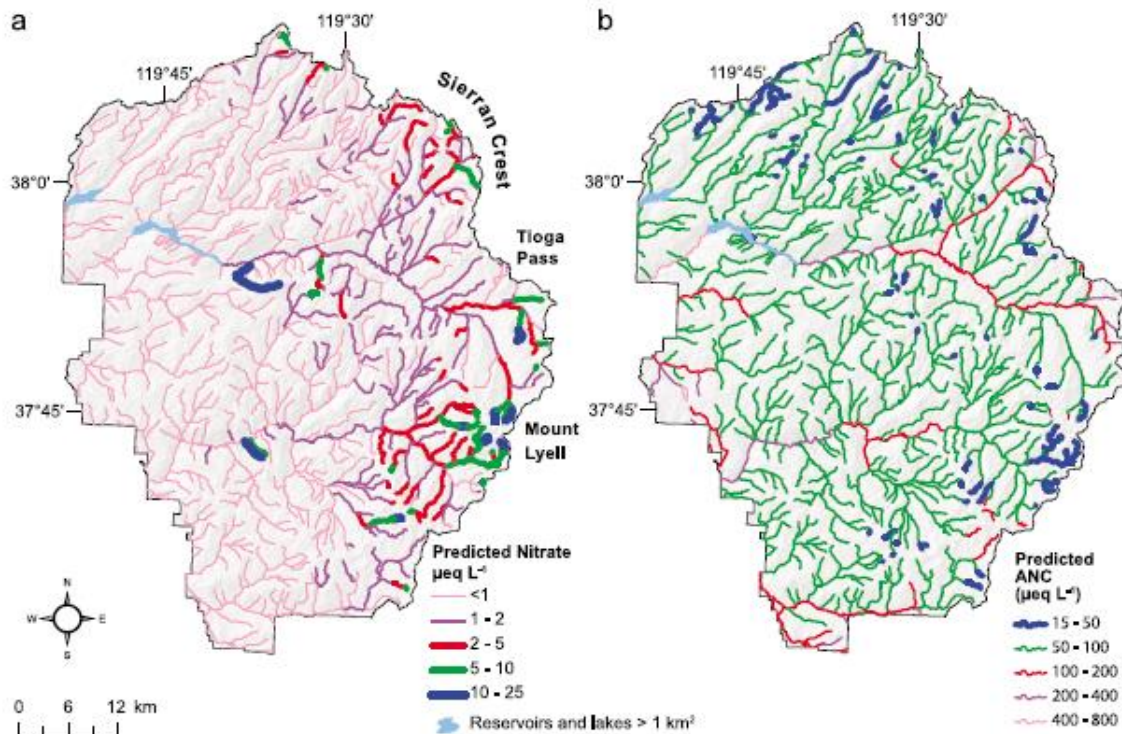
Temporal variability in surface water and soil solution chemistry, and patterns in nutrient uptake by terrestrial and aquatic biota, influence acidification processes and pathways. Thus, conditions are constantly changing in response to episodic, seasonal, and inter-annual cycles and processes. In particular, climatic fluctuations that govern the amount and timing of precipitation inputs, snowmelt, vegetative growth, depth to groundwater tables, and evapoconcentration of solutes influence soil and surface water chemistry and the interactions between pollution stress and sensitive aquatic and terrestrial biological receptors. Because of this variability, many years of data are required to establish the existence of trends in surface water chemistry. Assignment of causality to changes that are found to occur is even more difficult. The data that would be needed for determining the extent and magnitude of episodic acidification have not been collected to a sufficient degree in acid-sensitive areas of the SIEN parks to support regional assessment of episodic acidification.

Available data from intensive study sites suggest that episodic depression of stream pH may be more pronounced than for lakes. Spatial variability can be considerable in lakes, and this complicates efforts to quantify the magnitude of episodic effects (Gubala et al. 1991). Moreover, synoptic lake surveys are typically conducted during the summer or autumn "index period," during which time lakewater chemistry exhibits low temporal variability. Although summer or autumn is an ideal time for surveying lakewater chemistry in terms of minimizing variability, lakewater samples collected during low-flow conditions provide little relevant data on episodic processes, and in particular on the dynamics or importance of N as an agent of acidification. Nitrate concentrations in lakewater are elevated during the growing season only in lakes having watersheds that exhibit fairly advanced symptoms of N saturation (Stoddard 1994).

In the Sierra Nevada, the hydrology of alpine and subalpine ecosystems is dominated by snowfall and snowmelt, with over 90% of the annual precipitation falling as snow. The relatively small loads of acidic deposition can supply relatively high concentrations of SO_4^{2-} and NO_3^- to lakes and streams during the early phase of snowmelt (Stoddard 1995) through the process of preferential elution (Johannessen and Henriksen 1978). Acidic deposition can contribute to episodic acidification of surface water both by supplying N which can produce pulses of NO_3^- during high flow periods, contributing hydrologically mobile SO_4^{2-} , and by lowering baseline pH and ANC, so that episodes that do occur are sufficient to produce biologically harmful conditions (Stoddard et al. 2003).



Map 10. Map of estimated relative sensitivities to acid deposition in YOSE on the basis of surficial and bedrock geology. Geologic data are from Huber et al. (1989). (Source: Clow et al. 2010)



Map 11. Maps of (a) predicted fall season surface water nitrate concentrations, and (b) predicted fall season surface water ANC in streams in YOSE (Source: Clow et al. 2010)

Lakewater pH and ANC in the Sierra Nevada generally decrease with increasing runoff, reaching minima near peak snowmelt discharge. Most other solutes exhibit temporal patterns that indicate dilution or a pulse of increased concentration followed by either dilution or biological uptake (Melack et al. 1998). In a study by Melack (1998), NO_3^- peaks of 5 to 15 $\mu\text{eq/L}$ were common, although they were usually less than 2 $\mu\text{eq/L}$ in the N-limited lakes (Chrystal and Lost Lakes). Increases in SO_4^{2-} concentration were smaller in magnitude. Except in watersheds thought to have bedrock sources of S (Spuller and Ruby Lakes), the differences between SO_4^{2-} maxima and minima were generally within 2 $\mu\text{eq/L}$. Nitrate and SO_4^{2-} then declined at peak runoff. Outflow ANC declined by 24 to 80% during the spring, with an average decline of 50%. Lowest ANC was generally between about 15 $\mu\text{eq/L}$ (Lost and Pear Lakes) and 30 $\mu\text{eq/L}$ (Ruby and Crystal Lakes). Seasonal ANC depressions were greatest during years with deep snowpacks and high snowmelt runoff (Melack et al. 1998).

Melack et al. (1998) found that the relationship between minimum ANC during snowmelt and fall overturn ANC in the Sierra Nevada was linear:

$$\text{minimum ANC} = (0.88 \pm 0.03) \times (\text{overturn ANC}) - (8.6 \pm 2.8)$$

$$(r^2 = 0.98, \text{ se} = 8.0 \mu\text{eq/L})$$

Application of this equation to the population of lakes in the Sierra Nevada that were included in the WLS statistical frame suggested that none of the lakes represented by the WLS were acidified to ANC below 0 $\mu\text{eq/L}$ by snowmelt under ambient levels of acidic deposition (Melack et al. 1998). However, the confidence limit of this empirical relationship allowed the possibility that up to 1.8% of lakes in the Sierra Nevada were acidified to ANC $\leq$ 0 $\mu\text{eq/L}$ during snowmelt.

Melack et al. (1998) reported the chemistry of the Emerald Lake outflow for the period 1983 through 1994. No trend was found in either pH or ANC during that time period, although NO_3^- concentrations declined after about 1990. Peak NO_3^- values in the lake outlet during 1983 through 1987 were above 10 $\mu\text{eq/L}$ in nearly all years, but only 8 to 9 $\mu\text{eq/L}$ during later years 1990 through 1994. Melack et al. (1998) hypothesized that climatic changes, for example the 1987-1992 drought, may have altered biological N uptake rates and therefore runoff concentrations of NO_3^- .

Williams and Melack (1991) and Williams et al. (1995) documented ionic pulses (2 to 10 days in duration) in meltwater concentrations in the Emerald Lake watershed twofold to twelvefold greater than the snowpack average. Sulfate and NO_3^- concentrations in meltwater decreased to below the initial bulk concentrations after about 30% of the snowpack had melted. The initial meltwater draining from the snowpack had concentrations of NO_3^- and NH_4^+ as high as 28 $\mu\text{eq/L}$, compared to bulk snowpack concentrations $< 5 \mu\text{eq/L}$ (Williams et al. 1995). Streamwater NO_3^- concentrations peaked during the early snowmelt period, with maximum streamwater concentrations of 18 $\mu\text{eq/L}$. During summer, streamwater NO_3^- concentrations were always near or below detection limit.

Stoddard (1995) reported the episodic acid-base chemistry of two lakes in the Sierra Episodes Study, one of which (Treasure Lake) typified the response of the majority of high elevation lakes in the study and one whose response was extreme (High Lake). At Treasure Lake, ANC began to decline at the onset of snowmelt and reached a minimum at peak runoff, corresponding with minimum base cation, NO_3^- , and SO_4^{2-} concentrations. The lakewater did not become acidic. High Lake watershed contained a deeper snowpack, and began melting later in the season. ANC fell to 0 or lower twice during the first 10 days of snowmelt. The ANC minimum corresponded with maximum concentrations of base cations, NO_3^- and Al. Nitrate concentrations increased to values greater than 40 $\mu\text{eq/L}$, exceeding concurrent increases in base cations and causing the lake to become acidic for brief periods. Stoddard (1995) concluded that High Lake appeared to be representative of the most extreme conditions of episodic acid-sensitivity in the Sierra Nevada.

Leydecker et al. (1999) investigated episodic lake acidification from 1990 to 1994 in seven high-elevation lake watersheds in the Sierra Nevada Mountains, including three lakes in Sequoia NP (Emerald, Pear, Topaz). Base cation dilution accounted for 75-97% of the episodic ANC depression during snowmelt. Where increasing anion concentration was important, SO_4^{2-} and NO_3^- were equal contributors during early snowmelt, and SO_4^{2-} predominated during late snowmelt. A model based on the observed relationship between snowmelt minimum and fall season ANC estimated that none of the lakes sampled in the Sierra Nevada during the WLS had been subject to episodic acidification to $\text{ANC} \leq 0 \mu\text{eq/L}$ (Leydecker et al. 1999).

Episodic acidification is often the limiting condition for aquatic organisms in streams that can be suitable for aquatic life under baseflow conditions. Potential biological effects of acidic deposition on surface waters in the Sierra Nevada are primarily associated with possible acidification from high NO_3^- concentration. In general, such effects tend to be episodic, rather than chronic.

Effects on Aquatic Biota

The aquatic biota most likely to show rapid eutrophication effects from N deposition are algae. Studies have shown an increase in lake phytoplankton biomass with increasing N deposition in not only the Sierra Nevada (Sickman et al. 2003), but also the Snowy Range in Wyoming (Lafrancois et al. 2003), Sweden (Bergström et al. 2005), and across Europe (Bergström and Jansson 2006). Increases in algal biomass have been associated with changes in algal assemblages that favor certain species over others. A widespread increase in the relative abundance of *Asterionella formosa* and *Fragilaria crotonensis* has occurred in oligotrophic lakes across the western United States; these changes have been documented from both lake sediments and limnological surveys (Goldman 1988, Interlandi et al. 1999, Saros et al. 2003, Wolfe et al. 2001). In Lake Tahoe, there has been a sharp increase in the ratio of araphidinate pennate diatoms to centric diatoms since about 1950 (largely due to increases in *Fragilaria crotonensis*), associated with increased N loading to the lake (Goldman 1988). Jassby et al. (1994) showed that atmospheric deposition supplies most of the N to Lake Tahoe.

Emerald Lake in Sequoia NP has been the focus of a considerable amount of work on potential biological effects of acidification due to S and N deposition. *In-situ* enclosure studies were conducted for 35 days at Emerald Lake by Barmuta et al. (1990). Contrary to previous studies (e.g., Melack et al. 1987), the lake sediments were included within the experimental enclosures. This allowed the investigators to document the response of zoobenthos as well as zooplankton. Treatments included a control (pH 6.3) and acid addition to reach pH levels of 5.8, 5.4, 5.3, 5.0, and 4.7. Results indicated that zooplankton were sensitive to acidification but zoobenthos were unaffected by the experimental treatment. *Daphnia rosea* and *Diaptomus signicauda* decreased in abundance below the range of pH 5.5 to 5.8 and were eliminated below about pH 5.0. *Bosnia longirostris* and *Keratella taurocephala* generally became more abundant with decreasing pH. Barmuta et al. (1990) concluded that even slight acidification of high-elevation lakes in the Sierra Nevada might alter the structure of the zooplankton community.

Melack et al. (1989) concluded that Emerald Lake was not showing serious chemical or biological effects of acidification. Many species of aquatic biota known to be acid-sensitive were found in Emerald Lake and associated streams, and the brook trout population did not show signs of acid-induced stress. However, Melack et al. (1989) also concluded that Emerald Lake and associated streams are extraordinarily sensitive to acidification because of their extremely dilute ionic chemistry. If acidic deposition was to increase in the future, stream biota would also likely be impacted. Seasonal patterns in the chemistry of Emerald Lake are controlled largely by thermal stratification, flushing during snowmelt, and nutrient uptake by phytoplankton during the ice-free season (Melack et al. 1989). Interannual variation in the chemistry of Emerald Lake and the streams in its watershed were largely explained by variation in the annual quantity of snowfall, which in turn

determines the degree of flushing of the lake during snowmelt and also the duration of the subsequent ice-free season.

Responses of aquatic macroinvertebrates to acidification were evaluated by Kratz et al. (1994) in 12 streamside channels in Sequoia NP. Replicated treatments included a control (pH 6.5 to 6.7) and experimental exposure at pH levels of 5.1 to 5.2 and 4.4 to 4.6. Invertebrate drift was monitored continuously and benthic macroinvertebrate densities were determined before and after acidification. Single 8-hr acid pulses increased the drift of sensitive taxa, and their densities were reduced. Mayflies (*Baetis* sp.) showed reduced density post-treatment to less than 25% of control densities in both pH reduction treatments (5.2, 4.6) and two different experimental exposures. Densities of *Paraleptophlebia* sp. appeared to be reduced by the acidification, but most treatment effects were not statistically significant. Kratz et al. (1994) suggested that the effects of acid inputs on benthic species densities depended on microhabitat preferences. *Baetis* sp. nymphs are epibenthic and active. They are often found on the upper surfaces of rocks where they are directly exposed to acidified water. This may have been responsible for their greater response to acidification.

In acid-sensitive lakes in the western United States, the focus of concern regarding biological effects of acidification is often mainly on native salmonid fish. It is important to note, however, that many high-elevation lakes and streams in the SIEN region were historically fishless. The top predators in such aquatic ecosystems were often amphibians or crustaceans. Thus, even though fish might be considered native to high-elevation waters in the SIEN region, they were not necessarily native to a particular lake or stream.

At least 30 non-native fish species have been introduced to Sierran waters, 10 of which have become widespread (Sullivan et al. 2001). Fish introductions have been especially pronounced at the higher elevations (> 1,800 m) which lacked any fish fauna prior to the trout introductions that began during the nineteenth century.

Serious declines and extirpation of frogs and toads have been documented in many areas of the United States. National parks in California have been affected, including YOSE and SEKI. Perhaps the greatest justification for focusing attention on amphibians in the high Sierra is that dramatic population declines appear to have already occurred or are in progress for at least two of the five amphibian species that still occur in the high Sierra (Bradford and Gordon 1992, Pierce 1985). These are mountain yellow-legged frog (*Rana muscosa*) and Yosemite toad (*Anaxyrus canorus* or *Bufo canorus*), both of which are restricted to high elevation. Many of the population declines of these species have occurred in seemingly pristine environments, including areas within SEKI, YOSE, and numerous wilderness areas in the SIEN region. Possible causes for these declines include acidic deposition, disease, habitat loss, increased ultra-violet light, climatic changes, toxics, or a combination of such factors (Boiano et al. 2005). The decline and extinction of amphibians has also apparently been aggravated at many locations by the introduction of non-native fish. Historically it was possible for amphibians to use streams as dispersal corridors. However, the presence of introduced fish in many of the Sierran lakes and streams greatly reduced or eliminated this possibility (Bradford et al. 1993). Predatory trout have dramatically altered lake and stream ecosystems and have been implicated in the decline of a number of amphibian species, in particular the pronounced

decline of the mountain yellow-legged frog, whose historic distribution corresponded very closely with location of the zone of historically fishless lakes and streams (Jennings 1996). Prior to the introduction of game fish, the mountain yellow-legged frog was probably the most prevalent aquatic vertebrate in mid and high-elevation lakes in the Sierra Nevada (Bradford 1989). Surveys have indicated, however, that the species disappeared from much of its former range (Bradford and Gordon 1992, Phillips 1990). Surveys for Yosemite toad have also indicated that it has disappeared from approximately half of its former range (cf., Bradford and Gordon 1992).

The sensitivity of aquatic amphibians to air pollution impacts is noteworthy for a number of reasons (Bradford and Gordon 1992). Many of the physiological and ecological characteristics of amphibians render them especially sensitive to environmental change or degradation (Blaustein and Wake 1990). Additionally, aquatic amphibians at high elevation in the Sierra Nevada breed during or shortly after snowmelt, and are exposed to the acidifying influence of the Sierran snowmelt during early life stages that are most sensitive to acidification (Freda 1990). Laboratory dose-response studies for the mountain yellow-legged frog, Yosemite toad, Pacific tree frog, and long-toed salamander (*Ambystoma macrodactylum*) showed high survival for all four species at higher pH levels, but survival declined dramatically as a function of pH in the mid to low 4s.

Bradford and Gordon (1992) studied several species of amphibian as potential indicators of adverse ecological effects of acidic deposition in the Sierra Nevada (see also Bradford et al. 1993, 1994). They conducted laboratory dose-response studies to determine the sensitivity of four amphibian species to low pH and elevated Al concentration in early life stages, and they also conducted field surveys to characterize the abundance and associated water chemistry of amphibian populations at high elevation. The results suggested that amphibians were at little risk from low pH in waters that might be acidified to pH 5.0. The authors concluded that the possibility exists that observed sublethal effects in response to pH as high as 5.25 might represent a threat to amphibian populations due to reduced growth rate and early hatching. Potential amphibian breeding sites were surveyed for two declining and one non-declining species at high-elevation within 30 randomly selected survey areas. No significant water chemistry differences were found between sites that contained the species versus sites that lacked the species. It appeared that the water chemistry was not different among the sites inhabited by the three species. These findings implied that acidic deposition was unlikely to have been a cause of amphibian population decline in the Sierra Nevada (Bradford and Gordon 1992, Bradford et al. 1993, Bradford et al. 1994). If acidification of high-elevation surface water does indeed play a role in the observed amphibian decline, such a role is likely highly episodic in nature.

Nutrient Nitrogen Enrichment

Aquatic Ecosystem Enrichment

Some freshwater aquatic ecosystems in the United States are sensitive to nutrient enrichment effects from atmospheric N deposition. In order to be sensitive to such effects, the lake or stream must be N-limited. Conventional wisdom previously held that most lakes and streams in the United States are P-, rather than N-, limited. However, more recent research suggested that this may not always be the case. Surveys of the literature of fertilization experiments and lake studies found that oligotrophic waters are commonly N-limited, especially undisturbed northern temperate or boreal lakes that receive low levels of atmospheric N deposition (Bergström et al. 2005, Elser et al. 2009a, Elser et al. 2009b). In more productive and less remote fresh waters, nutrient enrichment from N deposition does not necessarily stimulate productivity or changes in species composition because P is more commonly the limiting nutrient. Also, in many places with even minor levels of human disturbance, nutrient enrichment with both N and P due to non-atmospheric anthropogenic sources is common. There is increasing evidence from surveys and paleolimnological research suggesting that N limitation is common, or was common in many remote lakes prior to human settlement (Elser et al. 2009a).

Sullivan et al. (2011a) evaluated relative risk of nutrient enrichment from N deposition for all I&M networks nationwide. The coarse network rankings developed by Sullivan et al. (2011a) for nutrient N Pollutant Exposure, Ecosystem Sensitivity to nutrient N enrichment, and Park Protection yielded an overall network nutrient N enrichment Summary Risk ranking for SIEN parks that was highest among the 32 I&M networks. The overall level of concern for nutrient N enrichment effects on I&M parks within the SIEN was judged by Sullivan et al. (2011a) to be Very High.

The SIEN parks were ranked Low or Moderate in nutrient N enrichment Pollutant Exposure (Table 4). The somewhat higher levels of N deposition generally occur along the western edge of SEKI and YOSE (Fenn et al. 2010). Ecosystem Sensitivity to nutrient N enrichment for all three of the larger

Table 4. Estimated park rankings¹ according to risk of nutrient enrichment impacts on sensitive receptors (Source: Sullivan et al. 2011a)

Park Name ²	Park Code	Estimated Nutrient N Pollutant Exposure	Estimated Ecosystem Sensitivity to Nutrient N Enrichment
Devils Postpile	DEPO	Low	Low
<i>Kings Canyon</i>	KICA	Low	Very High
<i>Sequoia</i>	SEQU	Moderate	Very High
<i>Yosemite</i>	YOSE	Moderate	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 mi².

parks in this network was ranked in the highest quintile (Very High; Table 4), in part because all three parks contain numerous high-elevation lakes that might be more prone than lakes at lower elevation to N-limitation, and therefore potentially more susceptible to eutrophication in response to atmospheric N input. Additionally, there are large areas of potentially nutrient-sensitive vegetation in these parks, including grassland and meadow, arid and semi-arid, and alpine vegetation types. The predominant vegetation type within the parks in the SIEN that is thought to be highly sensitive to nutrient N enrichment is grassland and meadow. The screening study suggested that DEPO might be less sensitive to nutrient N enrichment. It was ranked in the second lowest quintile (Low) for Ecosystem Sensitivity to nutrient N enrichment (Table 4). 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.

An examination of EPA WLS data compiled by Eilers et al. (1987) found enhanced N concentrations in high elevation lakes adjacent to and downwind of urban centers (Fenn et al. 2003a). An additional survey of 62 lakes that were the subject of N-enrichment studies reported a mean increase in phytoplankton biomass of 79% in response to N-enrichment (average of 46.3 $\mu\text{eq/L N}$; Elser et al. 1990). Long-term measurements at Lake Tahoe, CA, to the north of the SIEN region, showed that primary productivity doubled, while water clarity declined, mostly as a result of atmospheric N deposition (Goldman 1988, Jassby et al. 1994). A meta-analysis of lakes from 42 regions of Europe and North America concluded that atmospheric N deposition was responsible for increased concentrations of N in lake water and elevated phytoplankton biomass (Bergström and Jansson 2006). Bergström et al. (2005) found a consistent pattern of nutrient limitation, showing N limitation for lakes that receive deposition below approximately 2.5 kg N/ha/yr, co-limitation of N and P for deposition between ~2.5 and 5.0 kg N/ha/yr, and P limitation in areas with N deposition greater than 5.0 kg N/ha/yr.

High-elevation lakes in the Sierra Nevada are primarily oligotrophic. Even small changes in the nutrient supply can impact algal productivity (Sickman et al. 2003) and cause important changes in other environmental parameters. Chamise Creek in SEKI was reported to have throughfall N deposition of 10 kg N/ha/yr and high NO_3^- leaching, suggesting relatively high atmospheric N loading and N saturation (Fenn et al. 2003a, Fenn et al. 2003c). The U.S. Forest Service has suggested policy thresholds for stream NO_3^- concentration in N-limited ecosystems in the western United States. A concentration less than 2 $\mu\text{eq/L}$ might suggest concern for possible over-enrichment of N (Fenn et al. 2011b).

Data from 28 Sierra Nevada lakes sampled in 1985 and again in 1999 suggested that NO_3^- concentrations decreased during that period and total P concentrations increased in more than 70% of the lakes sampled. Sickman et al. (2003) concluded that lakes throughout the Sierra Nevada appear to be experiencing measureable eutrophication in response to atmospheric deposition of nutrients, but N deposition is only part of the process.

At Emerald Lake, the concentration of NO_3^- during spring snowmelt runoff and during the growing season declined from 1983 through 1995 (Sickman et al. 2003). This was caused in part by changes in the snow regime; during the 1987-1992 drought, years having shallow and early-melting

snowpack had lower NO_3^- concentration in runoff due to decreased labile N production in soils and greater N uptake during longer plant growing seasons. Continued NO_3^- declines in lake water subsequent to the drought during the period 1993-2000 were likely caused by increased atmospheric P loading to the Emerald Lake watershed and the release of lake phytoplankton from previous P-limitation (Sickman et al. 2003). The authors also showed that these trends measured at Emerald Lake were reflected in the set of 28 Sierra Nevada lakes sampled in Sequoia NP and YOSE during synoptic lake surveys in 1985 and 1999. The most sensitive lakes are those located at high elevation (e.g., > 2400 m) and that are highly oligotrophic. Atmospheric deposition of both N and P represents a large fraction of the nutrient inputs to the watersheds of these lakes. Small changes in nutrient supply can therefore have substantial impacts on lake productivity.

Based on results of bioassay experiments and application of coarse nutrient limitation indices, Sickman et al. (2003) suggested that phytoplankton growth in Emerald Lake during the early 1980s was limited by P supply, but that there subsequently developed a pattern of co-limitation by N + P and N-limitation. The total P concentration in the lake doubled from 1983 to 1999. Particulate carbon (C) concentration in the lake in the autumn of 1999 was 4-fold higher than the average during the period 1983-1998. Together with the observed increase in total P, this shows that measureable eutrophication has occurred (Sickman et al. 2003). The authors further proposed that P loading has increased to most Sierra Nevada lakes, causing decreased NO_3^- concentration and greater incidence of N-limitation. The increased P loading may be due to increased emissions and deposition of P and/or accelerated internal P cycling due to changes in the timing of snowmelt and runoff patterns (Dettinger and Cayan 1995, Johnson 1998).

Sickman et al. (2001) calculated that the annual yield of N from the Emerald Lake watershed varied by a factor of 8 (0.4 to 3.2 kg N/ha/yr) and was a linear function of runoff, with runoff explaining 89% and 74% of the variation in dissolved inorganic and organic N, respectively. Ecosystem processes increased the N content of runoff during years having high runoff and reduced N losses during dry years. Nitrate pulses were larger during years having deep, late melting snowpacks. Thus, it is expected that a warming climate, with associated earlier snowmelt, might increase N retention in high-elevation watersheds in the Sierra Nevada (Sickman et al. 2001).

Because there was evidence of increased P loading throughout the Sierra Nevada, Sickman et al. (2003) concluded that site-specific P sources were unlikely to be the cause of observed trends. They proposed that atmospheric deposition and accelerated internal cycling of P in response to changes in climatic factors were the most likely sources of increased P loading to the Sierra Nevada Lakes. It is not known why atmospheric deposition of P to these lakes has increased over time. Possibilities include use of organo-phosphate pesticides (Kegley et al. 2000) and aeolian transport of soils and dust that are high in P from the San Joaquin Valley to the Sierra Nevada (Bergametti et al. 1992, Lesack and Melack 1996, Sickman et al. 2003). Research conducted at 1900 m elevation in Giant Forest, Sequoia NP showed that Fe/Al and Fe/Ca ratios suggested a mixture of mineral dust from regional agricultural activities and long-range transport of dust from Asia. Asian sources made up 40-90% in mid-summer and then declined during the late summer and early fall (Vicars and Sickman 2011).

Increased atmospheric deposition of N has the potential of altering the algal biomass of lakes in the Sierra Nevada to the extent that N is the growth-limiting nutrient in those lakes. To examine this issue, Sickman and Melack (1989) conducted experimental manipulations of the plankton in Emerald Lake *in situ* using artificial enclosures. Experiments were conducted using five microcosms (volume 10 L) and four mesocosms (volume about 3,500 L) during the summers of 1983 and 1984. These experiments were designed to determine the limiting nutrients for phytoplankton growth in Emerald Lake and separate out the effects of increased acidity from those of increased nutrient concentration on the lake's phytoplankton. Results suggested that phytoplankton growth in Emerald Lake was strongly limited by P at that time. Five out of seven experiments indicated that chlorophyll levels of the seston (algae and particulate matter in the water column) increased with P additions. Nitrogen was never found to be the sole limiting element and was co-limiting in only one experiment. The extent to which these results are applicable to other lakes throughout the Sierra Nevada is unclear.

Baron et al. (2011) synthesized critical loads of N deposition for protecting against nutrient enrichment of high-elevation lakes, including within the SIEN region. For sites in the Rocky Mountains of Colorado and Wyoming and the Sierra Nevada, relationships between both mean and peak annual NO_3^- concentration and N deposition suggested a critical load near 2 kg N/ha/yr to prevent NO_3^- leaching.

Fenn et al. (2011a) summarized data reflecting the relationship between atmospheric N deposition and stream NO_3^- concentration in chaparral vegetation in three areas of southern California: 1) San Dimas Experimental Forest in the San Gabriel Mountains (Meixner et al. 2006, Riggan et al. 1985, Riggan et al. 1994), 2) Devil Canyon watershed in the western San Bernardino Mountains (Fenn and Poth 1999, Meixner and Fenn 2004), and 3) Chamise Creek in SEKI (Fenn et al. 2003a, Fenn et al. 2003c). The concentrations of NO_3^- in streams located in chaparral watersheds in California are the highest reported in North America, with concentrations in some streams exceeding 200 $\mu\text{eq/L}$ (Fenn and Poth 1999, Fenn et al. 2003a, Fenn et al. 2003c, Fenn et al. 2011a, Riggan et al. 1985, Riggan et al. 1994). Evaluation of N saturation in chaparral must also consider the prevalence of fire in this ecosystem type. The stand-replacing fire interval is only about 40 to 60 years (Minnich and Bahre 1995). Much of the deposited N that has accumulated in the litter and above-ground vegetation is released to the atmosphere during fire, and fire contributes to pulses of NO_3^- in streamwater (Anderson and Poth 1989, Riggan et al. 1994). Much of the accumulated N in the mineral soil generally remains on-site after a fire (Fenn et al. 2011a).

Terrestrial Ecosystem Enrichment

Herbaceous plants in alpine communities, such as are found in SEKI and YOSE, are considered very sensitive to changes in N deposition. A combination of short growing season, strong seasonal variation in moisture and temperature, shallow and poorly developed soils, steep terrain, sparse vegetation, and low rates of primary productivity generally limit the N uptake and retention capacity of herbaceous plant species in alpine ecosystems (Burns 2004, Fisk et al. 1998). Alpine plant communities have also developed under conditions of low nutrient supply, in part because soil-forming processes are poorly developed, and this also contributes to their N-sensitivity. Alpine herbaceous plants are generally considered N-limited and changes in alpine plant productivity and

species composition have been noted in response to increased N inputs (Bowman et al. 2006, Vitousek et al. 1997).

Nitrogen cycling in alpine environments is strongly tied to variations in moisture regime (Bowman et al. 1993, Bowman 1994, Fisk et al. 1998). Blowing snow is transported across alpine landscapes by wind and tends to accumulate in certain depression areas. These areas receive much higher levels of moisture and winter season N deposition than other more wind-swept portions of the alpine environment (Bowman 1992). Fenn et al. (2003a) suggested that a substantial amount of N may leach through the snow during the initial phases of snowmelt in some alpine areas that accumulate substantial snowpack. It is these moist meadow areas that may be most affected by N deposition and that are most likely to show changes in plant species composition and impacts on N cycling (Bowman and Steltzer 1998).

Nutrient enrichment is also an important concern in forested ecosystems in SIEN parks. Future increases in the two most limiting resources in Sierran mixed-conifer forests (water and N) can potentially change the understory plant community and increase the risk of wildfire in response to understory fuels buildup (Fenn et al. 1998, Hurteau and North 2009, Witty et al. 2003). It is important to land managers to determine how such changes are likely to affect the distribution and abundance of rare species in the national parks. Hurteau and North (2009) assessed potential effects on mock leopardbane (*Arnica dealbata*), a listed sensitive species in YOSE. Increasing N deposition by experimental application of 12 kg N/ha/yr over a three-year period negatively affected mock leopardbane coverage.

The most notable effect of N deposition on vegetation in the Sierra Nevada is alteration of the lichen community (Bowman et al. 2011, Fenn et al. 2008). Lichen communities in chaparral and oak woodlands in parts of California have been substantially changed by atmospheric N deposition. These affected plant communities occur along the western edge of SEKI. Impacts on lichen distribution have been most evident in the southwestern portion of the Sierra Nevada, near the Tahoe Basin and Modoc Plateau, and within SEKI and YOSE (Bowman et al. 2011, Jovan and McCune 2006). However, the response of lichens to N has been confounded by simultaneous exposure to O₃ (Fenn et al. 2011a).

The critical load to protect lichens in the western Sierra Nevada has been estimated to lie in the range of 3.1 to 5.2 kg N/ha/yr (Bowman et al. 2011, Fenn et al. 2008). Fenn et al. (2008) concluded that community composition of epiphytic macrolichens begins shifting from oligotrophic to more mesotrophic species at around 3.1 kg N/ha/yr and shifts further to domination by eutrophic species above about 5.2 kg N/ha/yr. Oligotrophic lichens may be completely eliminated at N deposition near 10 kg N/ha/yr (Bowman et al. 2011)

Eutrophic lichen richness and abundance have been shown to decrease with NH₃ emissions and N deposition in the Central Valley (Jovan and McCune 2005, Jovan 2008). Fenn et al. (2011a) reported that, of the 53 lichen survey sites in California that had relatively clean air scores, only three occurred in locations where the modeled deposition was more than 5.5 kg N/ha/yr.

Jovan and McCune (2006) developed a model of NH_3 exposure in forests of the Sierra Nevada. Non-metric multidimensional scaling was used to extract gradients in lichen community composition from surveys at 115 sites. The observed lichen communities suggested relatively high NH_3 deposition to forests of the southern Sierra Nevada, including portions of YOSE and Sequoia NP.

Fenn et al. (2008) examined eutrophication responses attributable to N deposition to ponderosa pine forests in California. Epiphytic lichens were used as bioindicators of N effects (Blett et al. 2003, Bobbink et al. 2003, Fenn et al. 2003a). Fifteen of the 24 study sites were located in the Sierra Nevada and 9 in the San Bernardino Mountains. Lichen species were classified into three groups based on their responses to atmospheric deposition of N (Geiser and Neitlich 2007, Jovan and McCune 2006, Jovan 2008). Acidophytes are sensitive to small increases in N deposition (Van Herk et al. 2003), and can be eliminated from the lichen community at moderate levels of N deposition. This group includes beard lichens (e.g., *Bryoria fremontii*) and other species used by wildlife for forage and nesting material in the Sierra Nevada (McCune et al. 2007). Neutrophytes are more tolerant of N input. Nitrophytes are fast growing, respond to increased NH_3 deposition, and favor high pH substrates, including the bark of hardwood trees.

Pardo et al. (2011b) identified the empirical CLs that would protect sensitive resources in Level I ecoregions across the conterminous United States against effects caused by atmospheric N deposition. If current deposition is lower than the CL for a given receptor, one would not expect harmful effects to occur. If current deposition exceeds the CL, the risk of harmful effects increases. Some parks may be included in more than one ecoregion, so CLs for the same receptor may vary within a park. Data compiled by Pardo et al. (2011b) suggest that ambient N deposition may exceed the lower limit of the expected CL to protect against nutrient enrichment effects in some of the parks in the SIEN, mainly SEKI, and to a lesser extent, YOSE. Potential CL exceedances were reported for the protection of mycorrhizal fungi, lichens, herbaceous plants, and forest vegetation and to limit NO_3^- leaching in drainage waters (Table 5).

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 was generally estimated for protection of lichens (Geiser et al. 2010). Changes to lichen communities may signal the beginning of other changes to the ecosystem that might affect structure and function (Pardo et al. 2011a). Ellis et al. (2013) estimated the N CL for SEKI and YOSE in the range of 2.5-7.1 kg N/ha/yr for protection of lichens.

Ozone Injury to Vegetation

The O₃-sensitive plant species that are known or thought to occur within SIEN parks are listed in Table 6. Those considered to be bioindicators, because they exhibit distinctive symptoms when injured by O₃ (e.g., dark stipple), are designated by an asterisk. Each park in the SIEN contained at least six O₃-sensitive and/or bioindicator species.

Air pollution injury in California, especially that associated with exposure of sensitive plants to O₃, varies from virtually none in NPS networks to the north and northwest to significant within the SIEN, especially in SEKI (Sullivan et al. 2001) and substantial in the Los Angeles Basin. Campbell et al. (2007) documented O₃-induced foliar injury in 25 to 37% of Forest Inventory and Analysis (FIA) monitoring biosites in forested ecosystems in California during the period 2000 to 2005.

There have been more vegetation monitoring and research activities related to air pollution at SEKI than at any other western national park (Sullivan et al. 2001). The most comprehensive O₃ research has been conducted in the mixed conifer forest (Horner and Peterson 1993, Miller et al. 1989, Peterson et al. 1987, Peterson et al. 1991, Peterson et al. 1992a, Peterson et al. 1992b), in part because of the known high sensitivities of ponderosa pine, Jeffrey pine, and quaking aspen (*Populus tremuloides*). Fewer data are available to relate O₃ dose or exposure to mature trees or herbaceous plant species in this network.

Table 5. Critical loads for nitrogen in the SIEN, determined by ecoregion and receptor from Pardo et al. (2011b). Ambient N deposition reported by Pardo et al. (2011b) is compared to the lowest critical load for a receptor to identify potential exceedance, indicated by graying. A critical load exceedance suggests that the receptor is at increased risk for harmful effects.

NPS Unit	Ecoregion	Modeled N Deposition (kg N/ha/yr)	Critical Load (kg N/ha/yr)				
			Mycorrhizal Fungi	Lichen	Herbaceous Plant	Forest	Nitrate Leaching
Devils Postpile NM	Northwestern Forested Mountains	2.2	5 - 10	2.5 - 7.1	4 - 10	4 - 17	4 - 17
Sequoia / Kings Canyon NP	Mediterranean California	6.6	7.8 - 9.2	3.1 - 6	6 - 33	17 - 39	10 - 17
Sequoia / Kings Canyon NP	Northwestern Forested Mountains	6.6	5 - 10	2.5 - 7.1	4 - 10	4 - 17	4 - 17
Yosemite NP	North American Deserts	3.7	NA	3.0	3 - 8.4	NA	NA
Yosemite NP	Northwestern Forested Mountains	3.7	5 - 10	2.5 - 7.1	4 - 10	4 - 17	4 - 17

Table 6. Ozone-sensitive and bioindicator plant species known or thought to occur in the I&M parks of the SIEN. (Data Source: E. Porter, National Park Service, pers. comm., August 30, 2012); lists are periodically updated at <https://irma.nps.gov/NPSpecies/Report>.

Species	Common Name	Park		
		DEPO	SEKI	YOSE
<i>Amelanchier alnifolia</i> var. <i>pumila</i>	Saskatoon serviceberry			x
<i>Apocynum androsaemifolium</i> *	Spreading dogbane	x	x	x
<i>Apocynum cannabinum</i>	Dogbane, Indian hemp		x	x
<i>Artemisia douglasiana</i> *	Mugwort	x	x	x
<i>Physocarpus capitatus</i> *	Ninebark		x	x
<i>Pinus jeffreyi</i> *	Jeffrey pine	x	x	x
<i>Pinus ponderosa</i> *	Ponderosa pine		x	x
<i>Populus tremuloides</i> *	Quaking aspen	x	x	x
<i>Quercus kelloggii</i>	California black oak		x	x
<i>Rhus trilobata</i> *	Skunkbush		x	x
<i>Rubus parviflorus</i>	Thimbleberry		x	x
<i>Salix gooddingii</i>	Gooding's willow		x	
<i>Salix scouleriana</i> *	Scouler's willow	x	x	x
<i>Sambucus mexicana</i> *	Blue elderberry	x	x	x
<i>Vitis vinifera</i> *	European wine grape		x	

* Bioindicator species

Giant sequoia seedlings in Sequoia NP are exposed to relatively high atmospheric O₃ levels and have been found to exhibit visible O₃ damage. Grulke and Miller (1994) investigated the effects of O₃ exposure on the gas exchange characteristics of giant sequoia trees of different ages using open top and branch exposure chambers. Seedlings were sensitive to O₃ exposure until they reached the age of about five years, after which low conductance, high water use efficiency, and compact mesophyll all contributed to natural O₃ tolerance (Grulke and Miller 1994).

Ozone Exposure Indices and Levels

The W126 and SUM06 exposure indices calculated by NPS staff are given in Table 7, along with Kohut's (2007) O₃ risk ranking. The two ranking systems differ in significant ways. The NPS ranking system (NPS 2010) is a quick assessment of O₃ condition and simply ranks O₃ exposure levels according to injury thresholds from the literature (Heck and Cowling 1997), using a 5-year average of the W126 (a measure of cumulative O₃ exposure that preferentially weights higher O₃ concentrations) or the SUM06 (a measure of cumulative O₃ exposure that includes only hourly concentrations over 60 ppb) metrics over a 3-month period. NPS (2010) classified the W126 as Moderate at values between 7 and 13 ppm-hr. Values higher than 13 ppm-hr were classified as High, and values lower than 7 ppm-hr were classified as Low. The SUM06 was classified as Moderate at values between 8 and 15 ppm-hr. Higher and lower values were classified as High and Low, respectively.

Table 7. Ozone assessment results for I&M parks in the SIEN based on estimated average 3-month W126 and SUM06 ozone exposure indices for the period 2005-2009 and Kohut's (2007) ozone risk ranking for the period 1995-1999¹.

Park Name	Park Code	W126		Sum06		Kohut O ₃ Risk Ranking
		Value (ppm-hr)	Ranking	Value (ppm-hr)	Ranking	
Devils Postpile	DEPO	32.25	High	34.32	High	High
Kings Canyon	KICA	40.39	High	51.20	High	High
Sequoia	SEQU	42.62	High	54.42	High	High
Yosemite	YOSE	27.77	High	29.80	High	High

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

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

Ozone levels have been high for many years at all of the monitoring sites in SEKI. The annual daily 1-hour maximum exceeded the state standard (90 ppb) in every year that data were available for the analysis reported by Sullivan et al. (2001), and regularly exceeded the federal standard (120 ppb). Passive O₃ samplers showed that the highest O₃ levels occurred in the western portions of Sequoia NP, adjacent to the San Joaquin Valley.

At 13 sites in YOSE where O₃ was monitored, measurements rarely exceeded the federal one-hour O₃ standard (120 ppb) between 1988 and 2013, but the California O₃ standard of 90 ppb was exceeded at all sites (cf., Sullivan et al. 2001). Bytnerowicz et al. (2013) reported one exceedance of the 8-hour average concentration primary federal O₃ standard (75 ppb) during 2007 (a low fire year) and three exceedances during 2008 (a high fire year) at DEPO.

NPS (2010) evaluated the fourth-highest 8-hour O₃ concentrations for national parks that have consistently been at or above the standard of 75 ppb, based on 11-20 years of monitoring data running through 2008. There were six parks that routinely had such high concentrations, including SEKI and YOSE.

A high seasonal average O₃ concentration was measured by Bytnerowicz et al. (2002) at Three Pole Corner (71.5 ppb) at mid-elevation in the lower Kaweah/Marble Fork drainage in Sequoia NP. At higher elevation and increasing distance from the San Joaquin Valley, O₃ concentrations decreased. Back trajectory analyses conducted by Burley and Ray (2007) suggested that air masses having high O₃ concentrations at YOSE often originate in the San Francisco Bay area and pass through the Central Valley prior to reaching YOSE.

Burley and Ray (2007) sampled atmospheric O₃ concentrations using portable O₃ monitors at multiple locations in YOSE during the summers of 2003 and 2005. The goal was to provide data that would help interpolate measurements from fixed monitoring stations at Turtleback Dome and Merced River to remote park locations in complex terrain. Most study sites exhibited similar O₃ exposure during well-mixed daytime periods. However, concentrations were more variable at night. The O₃ exposures tended to be highest in the western and southern portions of the park. As discussed below, sampled locations generally fell into one of two groups based on the magnitude of the observed diurnal variation in O₃ levels.

Some sites experienced frequent middle-of-the-night O₃ spikes, which suggested that they were well exposed to the free troposphere during the evening. Because the nocturnal O₃ levels tended to be high at such sites, their average exposures over a 24-hr period were generally 50 ppb or higher. Other sites typically had pre-dawn O₃ levels less than 50 ppb. They had few nocturnal O₃ spikes and were not well exposed to the troposphere during evening hours.

Wildfire and prescribed fire can also contribute NO_x, which can cause elevated O₃ concentrations. For example, Bytnerowicz et al. (2013) measured surface O₃ concentrations at DEPO during a low-fire year (2007) and a high fire year (2008). Mean and median values were similar, but maximum concentrations in June and August, 2008 were higher than the observed 2007 values. The increases during the high-fire year were attributed to O₃ precursor emissions from wildland fires, in addition to transport of polluted air from the Central Valley and San Francisco Bay Area. Back trajectory analyses showed lowest O₃ levels at DEPO when air masses originated over the Pacific Ocean and then moved West to East at high altitude; highest O₃ levels occurred when air masses originated near the San Francisco Bay Area and then moved toward the southeast.

U.S. EPA measurements of atmospheric O₃ concentrations at 568 monitoring sites nationwide in 2008 showed generally stable levels throughout the 1990s, with declines between 2002 and 2007 attributed largely to NO_x emissions reductions (U.S. EPA 2008). Even though there have been widespread improvements in atmospheric O₃ levels, there were still 51 sites classified as nonattainment areas in 2007 because of failure to meet the O₃ NAAQS. Some of the highest O₃ concentrations in the United States in 2007 were in California (U.S. EPA 2008).

The U.S. EPA proposed a new O₃ standard in January, 2010 (Federal Register Vol. 75, No. 11, 40 CFR Parts 50 and 58, National Ambient Air Quality Standards for Ozone, Proposed Rules, January 19, 2010, p. 2938). It was based on an index of the total plant O₃ exposure during the daytime, whereby hourly values were weighted according to magnitude and then summed, as the three-month period having the highest cumulative exposure. The proposed standard was based on a three-year

average of the annual W126 metric. EPA proposed to set the level of the new standard in the range of 7-15 ppm-hr. There were 17 parks that exceeded the upper end of this range in 2008. The highest values were reported for SEKI (57 ppm-hr), Joshua Tree NP (53 ppm-hr), YOSE (34 ppm-hr), and Death Valley NP (29 ppm-hr). All of these parks are located in California.

Ozone Formation

Ozone is a potential threat to high-elevation plant species because concentrations and total exposure can be higher at higher elevations under appropriate atmospheric conditions (Brace and Peterson 1996, 1998, Loibl et al. 1994, Sandroni et al. 1994). At some locations in the Sierra Nevada and southern California, O₃ concentrations and total exposure increase with elevation to 1200-1500 m, and then decrease at higher elevation (Bytnerowicz et al. 1999, Van Ooy and Carroll 1995).

Ozone Exposure Effects

Field Survey Results

High O₃ exposures in the SIEN region have affected trees in the parks. Lower montane forests in the SIEN region are dominated by ponderosa pine on xeric sites. Ponderosa pine is highly sensitive to O₃ exposure. At mid-elevation, mixed conifer forest is prevalent, including some ponderosa pine, along with white fir (*Abies concolor*), incense cedar (*Calocedrus decurrens*), sugar pine (*Pinus lambertiana*), and California black oak. Jeffrey pine replaces ponderosa pine within this forest type at higher locations and on shallow soils. The change from black oak woodland to ponderosa pine forest is abrupt at relatively dry sites at mid elevation. Lower montane forests are widespread on the west side of Sequoia NP and are dominated by ponderosa pine. Groves of giant sequoia (*Sequoiadendron giganteum*) are found at scattered locations mixed with various combinations of the other lower montane coniferous tree species.

Montane mixed coniferous forests are also widespread at lower to mid elevations in YOSE, from about 900 to 2,100 m elevation. They are dominated by ponderosa pine, sugar pine, incense cedar, white fir, and Douglas fir (*Pseudotsuga menziesii*), and occupy 21% of the park. Ponderosa pine dominates lower slopes and drier south-facing aspects, with typical high, open canopies and a sparse understory. In many areas, it is found mixed with the more shade tolerant incense cedar and white fir, as well as sugar pine, California black oak, and various shrub species. Prior to the 20th century, these stands burned more frequently and had a more open structure and lower stem density with a greater dominance by ponderosa pine. Groves of giant sequoia (*Sequoiadendron giganteum*) are found at scattered locations mixed with various combinations of the other lower montane coniferous species.

Upper montane coniferous forests vary considerably in species and stand structure. The upper montane zone is found between about 2,000 and 2,600 m elevation and occupies 23% of YOSE. Dry and rocky areas, especially on south-facing slopes, are occupied by Jeffrey pine. Jeffrey pine is found in the lower portion of this elevational band on well-drained soils and granitic ridges. Grulke et al. (2003) tested whether this species had different transpirational patterns (with associated differing O₃ uptake potential) in mesic versus xeric microsites in Sequoia NP. Based on leaf gas exchange measurements, trees on mesic sites had an estimated 46% decrease in O₃ uptake from June to August; trees on xeric sites had a 72% decrease over the same time period. Trees on mesic sites showed

greater O₃ injury, as indicated by lower foliar N content and reduced needle retention in mid-canopy (Grulke et al. 2003). The only deciduous tree that is common in the upper montane zone is quaking aspen (*Populus tremuloides*), which is found in dense stands near streams and other areas that have relatively high soil moisture.

Chaparral vegetation, which occurs at lower elevations along the western edge of SEKI, is relatively O₃-tolerant (Stolte 1982, Temple 1999). In addition, chaparral vegetation is quiescent during summer, when O₃ levels in some parts of southern California are relatively high (Fenn et al. 2011a).

Just as O₃ varies in magnitude spatially within the SIEN region, it has varying effects on different plant species. Field data suggest a shift in community composition with elevated O₃ concentration that favors grass species over legumes (U.S. EPA 2006b). A study by Weinstein et al. (2005) showed that white fir was relatively unaffected by O₃ as compared to ponderosa pine, which showed significantly reduced growth with increased O₃.

The mixed conifer forest at SEKI is part of a broad region of the Sierra Nevada that has significant impacts to vegetation from chronic exposure to O₃. Spatial patterns of O₃ injury and spatial and temporal patterns of tree growth in SEKI have been quantified in several studies. In addition, intensive physiological investigations have provided evidence to support clear cause-effect relationships.

One of the first studies to quantify O₃ injury to ponderosa pine and Jeffrey pine in SEKI was completed in the early 1980s (Warner et al. 1983). This study documented widespread foliar injury as part of a broader regional pattern encompassing adjacent national forests (Allison 1982, Pronos et al. 1978, Pronos and Vogler 1981). It motivated periodic surveys of oxidant injury to these bioindicator species at SEKI and YOSE (Duriscoe and Stolte 1989, Duriscoe 1990, Ewell and Gay 1993, Stolte et al. 1992). An extensive survey of sites along the western edge of SEKI (where O₃ exposure is highest) indicated that approximately 90% of pines had some evidence of foliar injury (including high injury on first-year needles), with symptomatic trees having lower needle retention than asymptomatic trees (Peterson and Arbaugh 1988, Peterson et al. 1991, Peterson and Arbaugh 1992). Injury at SEKI was higher than any other location in the Sierra Nevada. The Forest-Ozone Response Study (FOREST; Arbaugh et al. 1998) corroborated this pattern, determining that 93% of pines at SEKI had visible injury, again higher than at any other location in the Sierra Nevada. Physiological studies in and near SEKI in the field (Bytnerowicz and Grulke 1992, Grulke 1999, Patterson and Rundel 1989) and in controlled exposure studies of seedlings (Temple et al. 1992, 1993) confirmed that the observed injury was related to physiological effects in pines.

The FOREST study was conducted during 1991-1994. It quantified the distribution of O₃ injury to forest species throughout California (Arbaugh et al. 1998, Cahill et al. 1996, Rocchio et al. 1993). This study was linked to the Sierra Cooperative Ozone Impact Study (SCOIAS), another regional study that focused primarily on monitoring of ambient O₃ and associated weather variables in the Sierra Nevada (Van Ooy and Carroll 1995). The FOREST study added to the spatial resolution of long-term research and monitoring of O₃ effects by Miller (1992) and Miller and McBride (1999) and to extensive surveys of injury and growth patterns in the Sierra Nevada by Peterson et al. (1987,

1991) and Peterson and Arbaugh (1988, 1992). Other assessments of O₃ injury have been conducted for individual national forests and national parks (e.g., Pronos and Vogler 1981, Vogler 1982, Warner et al. 1983), but the FOREST results are more spatially comprehensive.

The FOREST study included O₃-injury surveys at 11 sites (all with associated monitoring data), ranging from Lassen Volcanic NP in northern California to San Bernardino National Forest in southern California, with sites distributed throughout the westside Sierra Nevada within the elevational range of mixed conifer forest. The FOREST study included two sites in YOSE and two sites in SEKI. Southern airsheds on the western slopes of the Sierra Nevada (SEKI and YOSE) experience elevated O₃ concentrations and N deposition, especially during summer months (Sullivan et al. 2001).

Visible O₃ injury to ponderosa pine and Jeffrey pine was detected at all FOREST sites, ranging from 26.8% of trees at the northernmost site to 100% at the southernmost. Mean whorl retention ranged from 6.5 to 2.7 for these same sites (although Jeffrey pine, which is more dominant in the north, has more needles than ponderosa pine). The computed Ozone Injury Index (OII; Schilling and Duriscoe 1996) ranged from 6.3 in the north to 65.1 in the south. It was determined that the OII was strongly correlated with the Forest Pest Management (FPM) injury index used by the Forest Service (Pronos et al. 1978), which indicated that data collected by personnel from different organizations could be combined for robust analyses. Most importantly, there were significant correlations between OII and various O₃ indices over the geographic range of the study. This suggested that (1) O₃-monitoring data could be used to predict O₃ injury in sensitive pine species and (2) injury data for pines (much less expensive to collect than ambient exposure data) provided a reasonable reflection of the level of O₃ exposure at a particular geographic location. This means that ponderosa pine and Jeffrey pine, which are present in several Class I national parks in California and elsewhere, can be used as true bioindicator species for O₃ sensitivity and exposure. The FOREST study was one of the first field studies to demonstrate a quantitative relationship between tree injury and cumulative O₃ exposure.

The FOREST study corroborated a previous analysis of O₃ injury (presence of chlorotic mottling and needle retention) to ponderosa pine in the Sierra Nevada (Peterson et al. 1991, Peterson and Arbaugh 1992). The study found a gradient of injury, ranging from low at northern sites (Tahoe National Forest) to high at southern sites (Sequoia NP and Sequoia National Forest); this study also included sites at YOSE. Again, strong correlations were found between injury level and exposure. Additionally, the 2006 O₃ Air Quality Criteria Document (AQCD; U.S. EPA 2006a) reported a causal relationship between O₃ exposure and decline in ponderosa and Jeffrey pine in the San Bernardino Mountains. Because these studies found essentially the same results using different methods at different points in time, one can have high confidence in the inference that O₃ injury increased from north to south in the Sierra Nevada and that the injury was directly proportional to ambient O₃ exposure. Reduced foliar biomass has been documented at SEKI and YOSE, and reduced photosynthetic rates and tree growth have been documented at SEKI.

Even more compelling evidence of the effects of O₃ on mixed conifer forest was provided by data that indicated that growth has been reduced in injured trees. Ewell (1989) and Duriscoe and Stolte (1992) found that the level of O₃ injury in ponderosa pine foliage was inversely correlated with foliar

biomass. Reduced stem growth was documented for both ponderosa pine and Jeffrey pine with O₃ injury in SEKI. Open-grown Jeffrey pine with injury symptoms were found to have 11% lower radial growth since 1950 as compared with uninjured trees from nearby locations (Peterson et al. 1987). As part of a study that examined tree growth at 56 sites ranging from the Tahoe National Forest in the northern Sierra Nevada to the Sequoia National Forest in the south, 8 sites (4 symptomatic, 4 asymptomatic) were examined at SEKI (Peterson et al. 1991, Peterson and Arbaugh 1992). Older trees and trees with lower needle retention tended to have the lowest growth. Prolonged exposure to elevated O₃ may have reduced root biomass in mature ponderosa pine (Grulke et al. 1998, Grulke 1999), which may have predisposed the trees to increased stress during periods of low soil moisture. Given that summer drought is a normal part of the Mediterranean climate of California, this could be a significant long-term stress.

SEKI consistently has been observed to have a high level of damage, with the most substantial effects occurring within the mixed conifer zone (Sullivan et al. 2001). Documentation of severe O₃ injury in dominant trees, reduced tree growth, and associated physiological data for mature trees in the western portion of SEKI presented a clear picture of widespread impacts from prolonged exposure to O₃ and other air pollutants.

YOSE has also experienced severe O₃-induced foliar injury to ponderosa pine. Ozone injury was widespread in the western portion of the park and foliar biomass was lower in symptomatic trees. YOSE is located adjacent to the San Joaquin Valley, which experiences high levels of O₃ during summer months. Concentrations of gases and particulate air pollutants are transported to the park from the valley by prevailing westerly winds. Ozone injury was first documented in YOSE by Duriscoe and Stolte (1989), and was followed up by another survey that determined that about 30% of the pines at four symptomatic sites had O₃ injury in needles that were two years old or less (Peterson et al. 1991, Peterson and Arbaugh 1992). The study of Arbaugh et al. (1998) found that about 40% of pines at two sites at YOSE had O₃ injury.

An analysis of tree growth at YOSE (Peterson et al. 1991, Peterson and Arbaugh 1992) found that the growth of symptomatic ponderosa pine was significantly lower since 1950, including trees with some of the largest growth reductions measured in the Sierra Nevada. However, two sites included in the YOSE study had growth decreases throughout the 20th century, with the most probable cause being annosus root rot, which is common throughout Yosemite Valley (Parmeter et al. 1978). The differential effects of O₃ and fungal pathogens on tree growth at YOSE are difficult to discern.

The Mediterranean climate that occurs at some moderate elevation locations in the Sierra Nevada, with its typical summer drought, limits foliar uptake of C and O₃ in ecosystems that contain ponderosa pine. Panek and Goldstein (2001) compared diurnal foliar patterns in young ponderosa pine trees in mixed conifer watered and control (natural drought) plots at moderate elevation (1300-1500 m) in the Sierra Nevada. When plant stomata are closed, O₃ flux into the leaf is reduced, even if ambient O₃ exposure remains high. Thus, increased rainfall enhances vulnerability to O₃ damage (Panek and Goldstein 2001). Estimated O₃ uptake per unit leaf area (O₃ atmospheric concentration times stomatal conductance) in the ambient drought stress plot was about 40% less than in the watered plot. Panek and Goldstein (2001) speculated that an important implication of this research is

that increased soil water availability, which might occur in the mixed conifer forests of California in the future, could make ponderosa pine trees vulnerable to O₃ damage at exposure levels that previously did not cause damage.

Model Responses

Weinstein et al. (2005) linked the TREGRO tree response and ZELIG community response models to simulate impacts of O₃ exposure (0.5, 1.5, 1.75, and 2.0 times ambient) on the growth and competitive success of white fir and ponderosa pine at three sites in California, including YOSE. The response of individual trees was modeled using TREGRO (Weinstein et al. 1991), based on results obtained for individual trees in controlled chamber studies. These results were then extrapolated to the overall forest using the ZELIG model (Urban 1990, Urban et al. 1991), which considers the effects of competition. Model results suggested little growth impact of O₃ on white fir, but substantial growth reduction for ponderosa pine. Under continued ambient exposure for 100 years, simulated ponderosa pine abundance decreased 16% at the most heavily polluted site (Crestline in the San Bernardino Mountains); the modeled decrease at YOSE was 10% (Weinstein et al. 2005).

Visibility Degradation

Natural Background Visibility and Monitored Visibility Conditions

The Clean Air Act set a specific goal for visibility protection in Class I areas: “the prevention of any future, and the remedying of any existing, impairment of 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 by 2064. Natural background visibility assumes no human-caused pollution, but varies with natural processes such as windblown dust, wildfire, volcanic activity and biogenic emissions. Visibility is monitored by the IMPROVE

network and typically reported using the haze index called the deciview¹ (dv). Lower dv values correspond with better visibility conditions. IMPROVE monitors are located in Sequoia NP and YOSE. The Sequoia NP monitor (SEQU1) is also used to characterize conditions at Kings Canyon NP.

Natural background visibility has been estimated by IMPROVE for Sequoia NP and YOSE (Table 8). Monitored visibility on the haziest days at 47 park locations reported by NPS (2010) during the period 2006-2008 ranged from 1.5 to 21 dv higher than the estimated natural background condition at each site.

Impaired visibility frequently occurs at SEKI, largely due to organics, sulfates, and nitrates. Visibility conditions vary by season. Smoke occasionally causes reduced visibility during the summer months.

Reconstructed extinction generated from aerosol data (Savig and Morse 2001) showed that the worst visibility occurred during summer, when the seasonal average visual range (VR; i.e., how far a person can see) was 60 km. Visibility impairment² at YOSE was largely due to organics and sulfates. Smoke from frequent fires typically reduces visibility during the summer months. Reconstructed extinction generated from the aerosol data at YOSE showed seasonal variation in visibility conditions. The best seasonal average VR (131 miles [211 km]) occurred during the winter months, and the worst seasonal average VR (67 miles [107 km]) occurred during the summer months. Emissions of organic aerosols from wildfire and biogenic emissions from vegetation in the SIEN region peaked during summer months in the baseline period 2000-2004 (Suarez-Murias et al. 2009).

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.

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

Table 8. Estimated natural background visibility and monitored visibility in SIEN parks averaged over the period 2004 through 2008.

Park Name	Park Code	Site ID	Estimated Natural Background Visibility		
			20% Clearest Days (dv)	20% Haziest Days (dv)	Average Days (dv)
Devils Postpile	DEPO	No Site			
Sequoia and Kings Canyon	SEKI	SEQU1	2.29	7.70	4.92
Yosemite	YOSE	YOSE1	0.99	7.64	4.08
Park Name	Park Code	Site ID	Monitored Visibility (For Years 2004 through 2008)		
			20% Clearest Days (dv)	20% Haziest Days (dv)	Average Days (dv)
Devils Postpile	DEPO	No Site			
Sequoia and Kings Canyon	SEKI	SEQU1	8.44	23.91	16.58
Yosemite	YOSE	YOSE1	3.10	16.99	9.73

Representative photos of selected vistas under three different visibility conditions are shown in Figure 1 for YOSE. Photos were selected to correspond with the clearest 20% visibility conditions, haziest 20% visibility conditions, and annual average visibility conditions at that location.

IMPROVE data indicate that air pollution at SEKI has reduced average natural visual range from 150 to 35 miles. On the haziest days, visual range has been reduced from 110 to 20 miles. Severe haze episodes occasionally reduce visibility to 5 miles. At YOSE, pollution has reduced average natural visual range from 160 to 75 miles. On the haziest days, visual range has been reduced from 110 to 35 miles. Severe haze episodes occasionally reduce visibility to 7 miles.

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 SO₂ 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. Soil can enter the atmosphere through both natural processes and human disturbance.

Figure 2 shows estimated natural (pre-industrial), baseline (2000-2004), and current (2006-2010) levels of haze and its composition for Sequoia NP and YOSE. The RHR requires at least three years of valid data out of a five-year period to calculate the five-year average for the baseline period (2000-2004). Sites having fewer than three years of valid data required use of the RHR_VS algorithm substitution to calculate the baseline. This process entailed using substituted valid data for 2002 and 2003 in Sequoia NP. For more information on this process, see

http://vista.cira.colostate.edu/improve/Data/IMPROVE/summary_data.htm.

The majority of the haze in Sequoia NP for the 20% haziest and average days was attributable to NO_3^- and organics (Figure 2), followed by SO_4^{2-} . On the clearest 20% visibility days, the contribution of SO_4^{2-} increased, and NO_3^- and organics continued to contribute substantially. The biggest difference between the 20% clearest and 20% haziest visibility days at Sequoia NP was the increased role played by NO_3^- on the 20% haziest days (Figure 2).

The majority of visibility impairment in YOSE on the 20% haziest and average days was attributable to organics (Figure 2). On the 20% clearest days, SO_4^{2-} was the largest contributor. The biggest difference between the 20% clearest and 20% haziest visibility days at YOSE was the increased role played by organics on the haziest days (Figure 2).

Analyses conducted by the Western Regional Air Partnership (WRAP) indicated that organics from natural emissions sources, including wildfire and biogenic sources (vegetation), contribute to substantial visibility impairment throughout the western United States, including within the SIEN region. In addition, air pollution sources outside the WRAP domain, including international off-shore shipping and sources from Mexico, Canada, and Asia, can in some cases be substantial contributors to haze (Suarez-Murias et al. 2009).

Some visibility impairment occurs at all of the National Park Service Class I monitoring sites in California (Sullivan et al. 2001). Monitoring data showed that coarse mass concentrations, particles between the size of 2.5 and 10 microns, were highest along the Pacific Coastal Mountains and lowest in the Sierra-Humbolt region. Fine aerosol concentrations were highest in the Southern California region. On an annual basis, organics contributed the most to light extinction at parks in the Sierra-Humbolt area (Lassen Volcanic NP) and Sierra Nevada area (YOSE and SEKI), whereas sulfates contributed the most to extinction in the Pacific Coastal Mountain parks (Pinnacles National Monument, Point Reyes National Seashore, Redwood NP), and nitrates were the largest contributors to extinction in southern California (Sullivan et al. 2001).

Yosemite

20% Clearest Days

Taken: 9:00 AM

Haze = 6 dv

$B_{\text{ext}} = 19 \text{ Mm}^{-1}$

VR = 210 km



20% Haziest Days

Taken = 9:00 AM

Haze = 17 dv

$B_{\text{ext}} = 56 \text{ Mm}^{-1}$

VR = 70 km



Average Days

Taken = 9:00 AM

Haze = 10 dv

$B_{\text{ext}} = 26 \text{ Mm}^{-1}$

VR = 150 km



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

SEKI

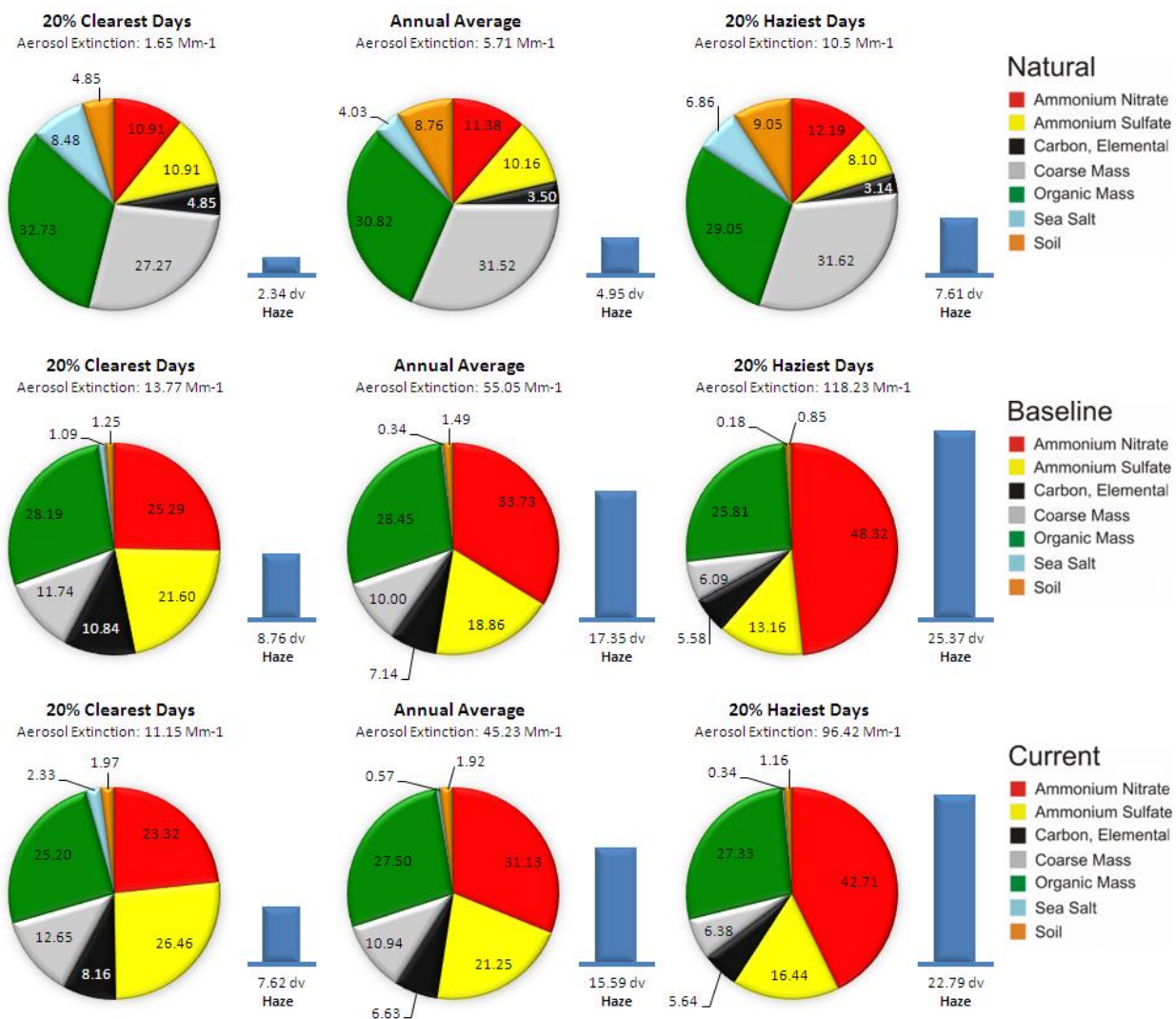


Figure 2a. Estimated natural (pre-industrial), baseline (2000-2004), and current (2006-2010) levels of haze (blue columns) and its composition (pie charts) on the 20% clearest, annual average, and 20% haziest visibility days for Sequoia NP. Sequoia NP has RHR2_VS substituted data for the years 2002 and 2003 (Data Source: NPS-ARD)

YOSE

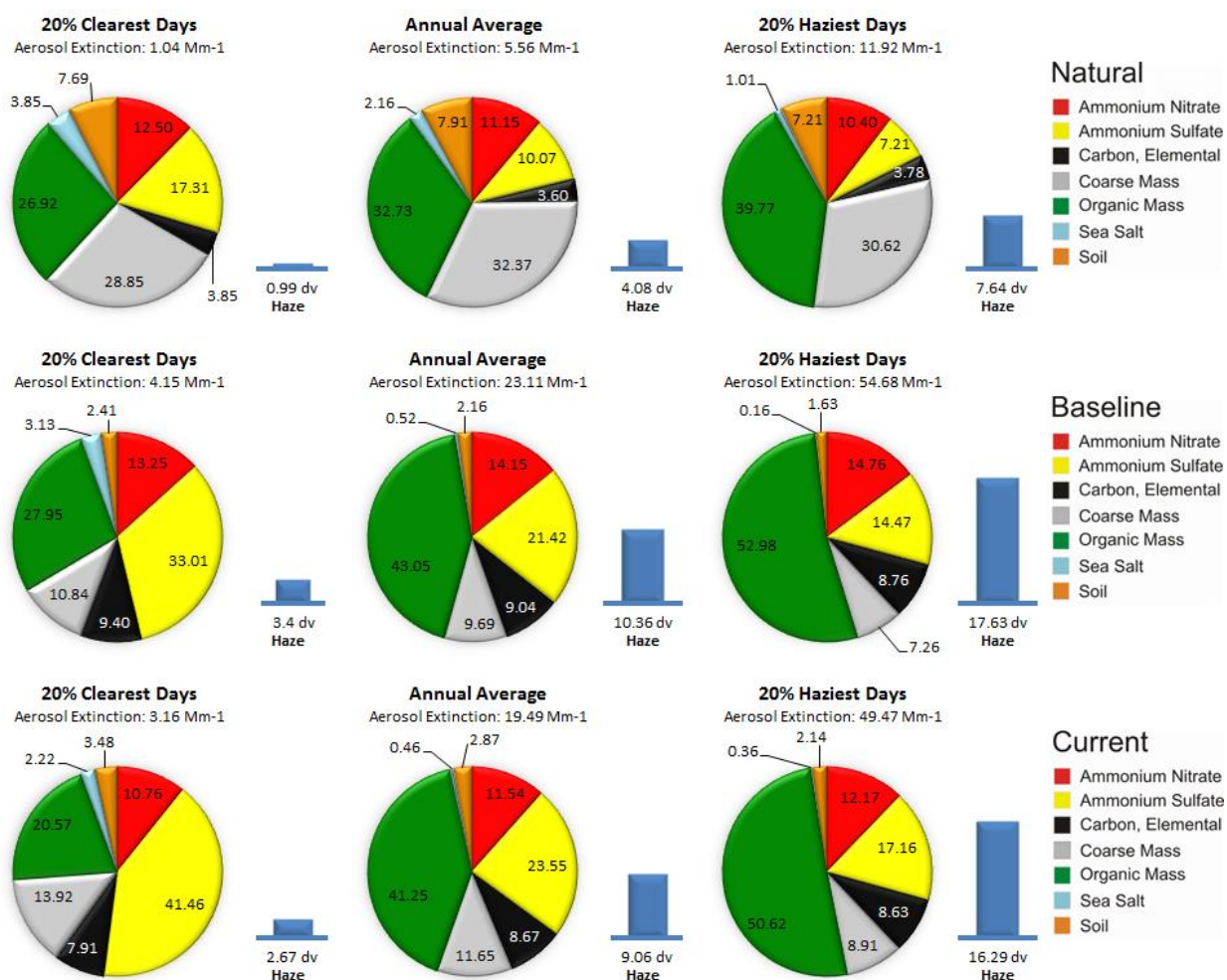


Figure 2b. Estimated natural (pre-industrial), baseline (2000-2004), and current (2006-2010) levels of haze (blue columns) and its composition (pie charts) on the 20% clearest, annual average, and 20% haziest visibility days for YOSE. Sequoia NP has RHR2_VS substituted data for the years 2002 and 2003 (Data Source: NPS-ARD)

Emissions of carbonaceous particles (organic C [OC] and elemental C [EC]) from wildfires can have strong and sustained regional impacts on aerosol concentrations, air quality, and visibility (McMeeking et al. 2006). This issue was investigated in YOSE as part of the Yosemite Aerosol Characterization Study (YACS), which was conducted during the summer of 2002 (McMeeking et al. 2005). Air masses arriving at YOSE were sampled to characterize visibility and to define aerosol sources contributing haze to the park. Results indicated that OC was the dominant aerosol species, especially during periods identified as smoke impacted. Meteorological conditions suggested that fires burning in Oregon had the largest impact on aerosol concentrations in YOSE during the study. Thus, it appears that emissions from regional wildfires can have substantial impacts on visibility in YOSE and other western park lands (McMeeking et al. 2006).

During the YACS study, there were several local wildfires and prescribed burns, in addition to two regional haze episodes that were strongly influenced by smoke from biomass burning that was transported long distances (Engling et al. 2006). Several types of biomass burning smoke tracers were used to quantify contributions of primary biomass burning smoke to $PM_{2.5}$. The fine aerosol in YOSE during the summer of 2002 was dominated by natural sources, mainly by smoke from wildfires and by secondary organic aerosols of biogenic origin (Engling et al. 2006). Low concentrations of anthropogenic organic compounds suggested that motor vehicles only contributed about 10%, on average, of the OC during that study.

There remains uncertainty regarding the quantitative role of organic carbon (OC) from smoke episodes and its influence on visibility. The primary objectives of the YACS was to characterize the physical, chemical, and optical properties of C-dominated aerosols. Results of YACS suggested that EPA's recommended approach for evaluating smoke-related light scattering, for tracking progress towards achieving the national visibility goal, may underestimate smoke-related light scattering by about a factor of two, if YOSE results are universally applicable.

Impairment on the 20% haziest days during the baseline period 2000-2004 was more than twice as high at Sequoia NP as compared with YOSE and with most other Class I areas in the Sierra Nevada (Suarez-Murias et al. 2009). The largest difference was for NO_3^- , which was responsible for about four times as much extinction in Sequoia NP, as compared with YOSE, on the 20% haziest days.

The baseline days having worst air quality were dominated by organic aerosols associated with biogenic emissions and wildfire. The monitor at Sequoia NP is situated at relatively low elevation (519 m), and is therefore in proximity to urban, agricultural, and transportation corridor emissions from the San Joaquin Valley that is located just west of the monitoring site. The Sequoia NP site requires a large reduction in haze in order to comply with the RHR by 2064 (Table 9).

Table 9. IMPROVE monitors and Visibility at Class I Areas in California. (Source: Suarez-Murias et al. 2009)

			Current Conditions (2000-2004 Baseline)		Future Natural Conditions (2064 Goals)		
Improve Monitor (name and elevation in meters)		Class I Area(s)	Worst Days	Best Days (maintain in future years)	Natural Worst Days	Deciview Hurdle (baseline to 2064)	Required Improvement from Current Visibility on Worst Days
BLIS (2131 m)	Bliss	Desolation Wilderness Mokelumne Wilderness	12.6	2.5	6.1	6.5	52%
HOOV (2561 M)	Hoover	Hoover Wilderness	12.9	1.4	7.7	5.2	40%
YOSE (1603 m)	Yosemite	Yosemite National Park Emigrant Wilderness	17.6	3.4	7.6	10.0	57%
KAIS (2598 m)	Kaiser	Ansel Adams Wilderness Kaiser Wilderness John Muir Wilderness	15.5	2.3	7.1	8.4	54%
SEQU (519 m)	Sequoia	Sequoia National Park Kings Canyon National Park	25.4	8.8	7.7	17.7	70%
DOME (927 m)	Dome :Lands	Dome Lands Wilderness	19.4	5.1	7.5	11.9	61%

Lightning is an important source of wildfire ignition in the SIEN region. Prescribed fire is also widely used for restoring and maintaining vegetation communities (Allen et al. 2002, Brockway et al. 2002, Fulé et al. 1997, McKenzie et al. 2006, Stephenson 1999). Managers of protected areas, such as national parks and wilderness, have adopted a policy whereby naturally ignited fires are managed for resource benefit when they do not threaten structures or ambient air quality (McKenzie et al. 2006, Miller and Landres 2004).

Smoke plumes can contribute to visibility impairment downwind from fire locations (Malm 1999). Fires have become more severe than they were historically, because of more extreme weather and buildup of fuel from previous fire suppression (Agee 1997, Allen et al. 2002, Covington 2000, Flannigan et al. 1998, McKenzie et al. 2006). This pattern may continue into the future in response to climate change. Both empirical (McKenzie et al. 2004) and process (Lenihan et al. 1998) models suggest that the area burned by wildfire is likely to increase in the western United States in response to a warming climate.

Source appointment analyses were conducted for the California Regional Haze Plan (Suarez-Murias et al. 2009), using regional-scale, three-dimensional air quality models that simulate emissions, chemical transformations, and transport of criteria air pollutants and fine particulate matter. Effects on visibility in Class I areas in California were then evaluated for organic C, SO_4^{2-} , and NO_3^- , which are the three major drivers of haze in California. The PM Source Apportionment Technology (PSAT) algorithm was used for WRAP model analysis. Directly emitted anthropogenic organic C was estimated to contribute half or less of the organic C in most areas of California. Anthropogenic sources of NO_x contributed at least half of the NO_3^- in all Class I areas in California except Redwood

NP (where it only contributed 7%). The anthropogenic SO_4^{2-} contribution ranged from 1 to 35% at various Class I areas, with highest contributions in southern California.

Trends in Visibility

Most of the investigated (Malm et al. 2002) national park sites in the western United States showed decreasing 20th percentile atmospheric SO_4^{2-} concentrations from 1989 to 1999. The trends were statistically significant at only 6 of 30 sites, including YOSE, where the reduction was about 40%.

No trend in dv was observed on the clearest or haziest 20% days for the visibility monitoring site in Sequoia NP during the period 1994-2008 (NPS 2010). However, visibility conditions in both Sequoia NP and YOSE show evidence of decreasing haze in recent years on the 20% clearest, average, and 20% haziest days (Figure 3). These apparent improvements in visibility have been most pronounced on the 20% haziest days since 2002.

Development of State Implementation Plans

According to the RHR, states and tribes must establish and meet reasonable progress goals for each federal Class I area to improve visibility on the 20% haziest days and to prevent visibility degradation on the 20% clearest days. The national goal is to return visibility in Class I areas to natural background levels by 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).

Glideslope analyses shown in Figure 4 suggest that haze levels on the 20% clearest days at both Sequoia NP and YOSE appear to be moving towards attainment of the national goal of natural background visibility by 2064 (~ 7.7 dv in each park). Rather large additional improvements will be needed for full compliance with the RHR. Additional monitoring will be needed.

Toxic Airborne Contaminants

In addition to criteria pollutants (O_3 , PM, NO_2 , SO_2 , and CO), a large number of chemical compounds can be found in ambient air monitoring samples at concentrations that are of concern from either a human health-effects or an environmental perspective. Among these compounds are a variety of pesticides, which are used extensively in California's heavily-farmed San Joaquin and Sacramento valleys. Pesticides vary as to their levels of volatility. Potential impacts are also affected by the degree to which a particular pesticide breaks down in the environment, and the levels of toxicity of the breakdown products. The release and transport of pesticides from their point of application to downwind areas involves numerous other important physical and chemical processes.

Although California only contains 3% of the agricultural land in the United States, it accounts for about 15% of all pesticide use (Census of Agriculture 2002), mostly in the Central Valley, which is generally upwind of the Sierra Nevada Mountains. The presence of pesticides in the bodies of Sierra Nevada amphibians is well documented (Cory et al. 1970, Datta et al. 1998, Fellers et al. 2004, Sparling et al. 2001). The disappearance of the mountain yellow-legged and other frog species from sites in California that they had occupied historically has been documented (Davidson et al. 2002, Davidson 2004, Davidson and Knapp 2007). The latter study quantified habitat characteristics and presence/absence of mountain yellow-legged frogs and fish at 6,831 sites in California. Upwind pesticide use was estimated from application records. After accounting for habitat effects, the probability of mountain yellow-legged frog presence was significantly reduced by both fish and pesticides, with the effect of pesticides much stronger than the effect of fish presence. These results suggest that windborne pesticides might contribute to amphibian decline in the Sierra Nevada (Bradford et al. 2011, Davidson and Knapp 2007).

The snowpack is efficient at scavenging both particulate and gas phase pesticides from the atmosphere. However, until recently, little was known about the occurrence, distribution, or sources of pesticides in alpine ecosystems. Analysis of pesticides in snowpack samples from seven national parks in the western U.S. by Hageman et al. (2006) illustrated the deposition and fate of 47 pesticides and their degradation products. Correlation analysis with latitude, temperature, elevation, particulate matter, and two indicators of regional pesticide use suggested that regional patterns in historic and current agricultural practices are largely responsible for the distribution of pesticides in the western national parks in the conterminous United States. Pesticide deposition to parks in Alaska was attributed to long-range atmospheric transport rather than regional sources (Hageman et al. 2006).

A known air pollution transport route into the Sierra Nevada is from the San Joaquin Valley. Some research indicates that pesticides used in the San Joaquin Valley may be transported into the Sierra Nevada. Pesticides applied to crops can volatilize under warm valley temperatures, and subsequently be transported via upslope air movement to be deposited in the cooler, high-elevation regions of the SIEN. Zabik (1993) demonstrated atmospheric transport of organophosphate pesticides from the Central Valley to two sites within Sequoia NP. The first site was located at Ash Mountain, at an elevation of 533 m. Organophosphate and other currently-used pesticides and polychlorinated biphenyls (PCBs) have been found in surface waters, fish, and amphibians at this location in Sequoia

NP (Datta et al. 1998). The second site was located at Lower Kaweah, in Giant Forest at an elevation of 1,920 m. A third site outside the park was located at a lower elevation, at the base of the Sierra Nevada foothills. Samples were collected of air and estimates were made of wet and dry deposition of pesticides during the winters of 1990-91 and 1991-92, and also during the spring of 1992. Zabik (1993) concluded that organo-phosphate compounds were detected in dry deposition but it appeared that wet deposition accounted for the majority of organophosphate insecticide deposition at all three of the sites during the winter months. The observed concentrations decreased substantially between Ash Mountain and Lower Kaweah (Zabik and Seiber 1993).

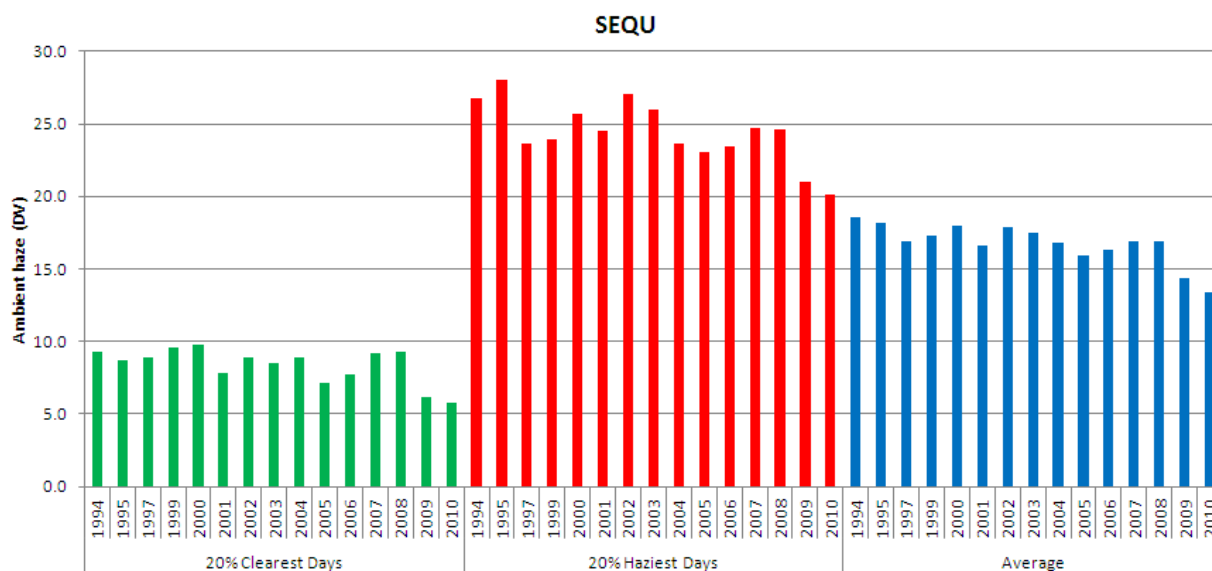


Figure 3a. Trends in monitored visibility at Sequoia NP, based on IMPROVE measurements on the 20% clearest, 20% haziest, and annual average visibility days over the monitoring period of record. Sequoia NP has RHR2_VS substituted data for the years 2002 and 2003. Data Source: http://vista.cira.colostate.edu/improve/Data/IMPROVE/summary_data.htm

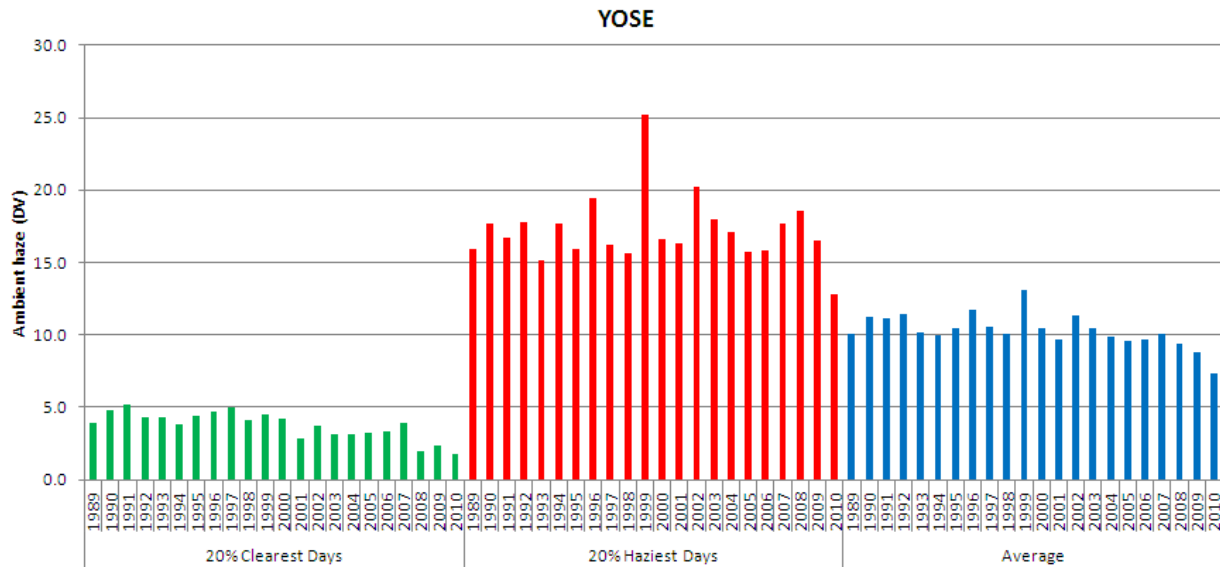


Figure 3b. Trends in monitored visibility at YOSE, based on IMPROVE measurements on the 20% clearest, 20% haziest, and annual average visibility days over the monitoring period of record. Sequoia NP has RHR2_VS substituted data for the years 2002 and 2003. Data Source: http://vista.cira.colostate.edu/improve/Data/IMPROVE/summary_data.htm

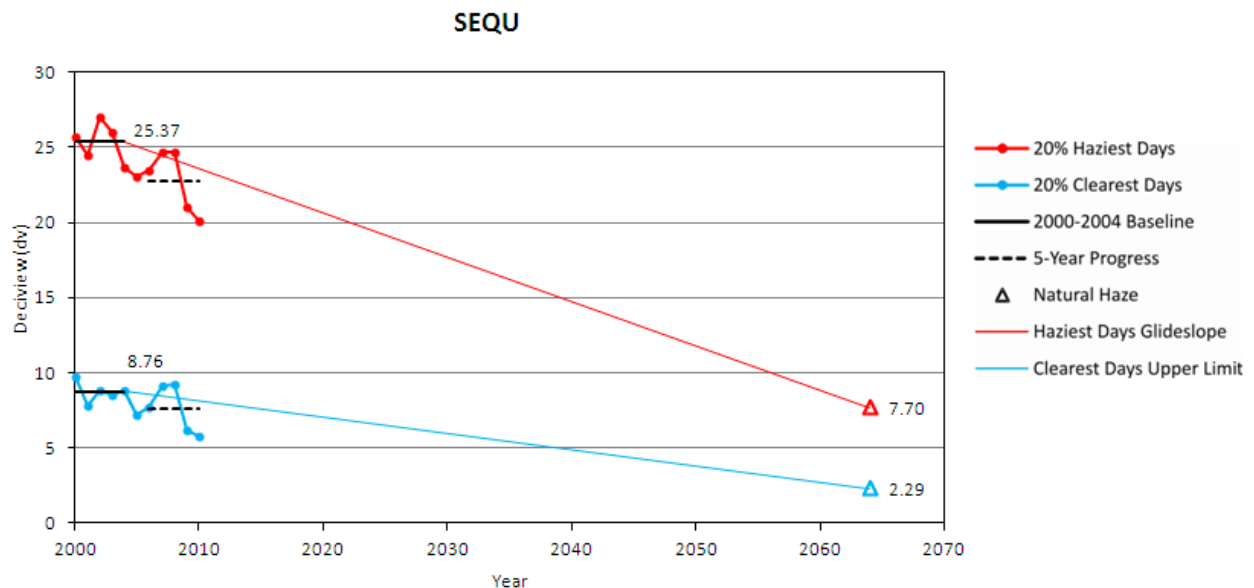


Figure 4a. Glideslopes to achieving natural visibility conditions by 2064 for the 20% haziest (red line) and the 20% clearest (blue line) days in Sequoia NP. In the Regional Haze Rule, the clearest days do not have a uniform rate of progress glideslope; the Rule only requires that the clearest days do not get any worse than the baseline period. Also shown are measured values during the period 2000 to 2010. Sequoia NP has RHR2_VS substituted data for the years 2002 and 2003. Data Source: http://vista.cira.colostate.edu/improve/Data/IMPROVE/summary_data.htm

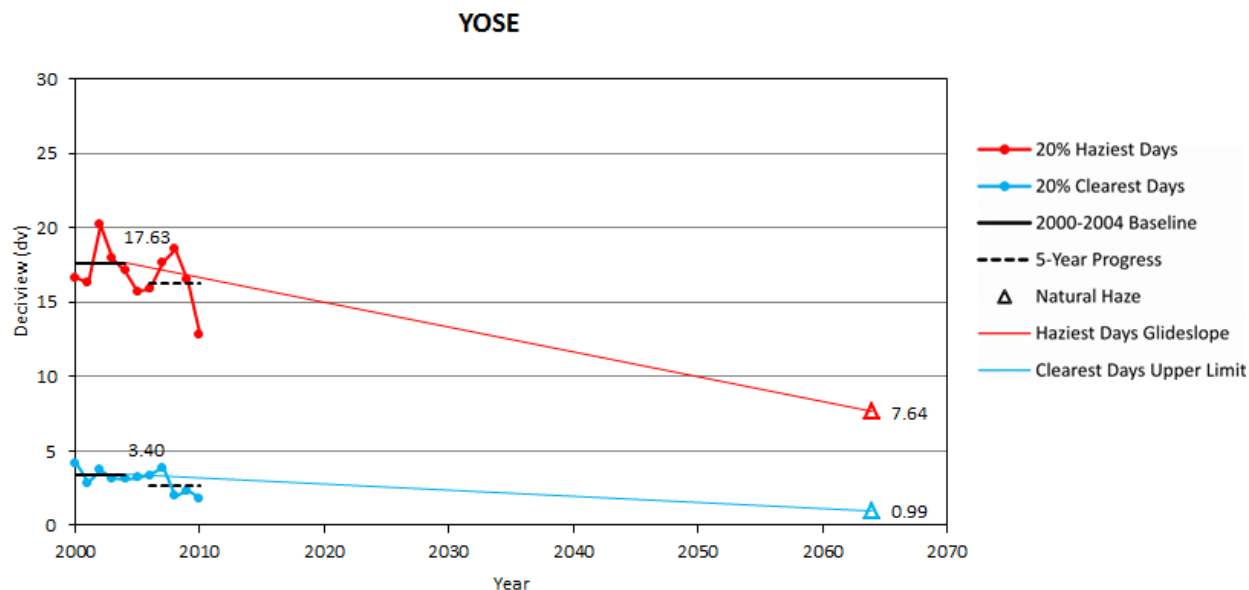


Figure 4b. Glideslopes to achieving natural visibility conditions by 2064 for the 20% hazeiest (red line) and the 20% clearest (blue line) days in YOSE. In the Regional Haze Rule, the clearest days do not have a uniform rate of progress glideslope; the Rule only requires that the clearest days do not get any worse than the baseline period. Also shown are measured values during the period 2000 to 2010. Sequoia NP has RHR2_VS substituted data for the years 2002 and 2003. Data Source: http://vista.cira.colostate.edu/improve/Data/IMPROVE/summary_data.htm

Air and dry deposition samples were collected during the period May to September, 1996 at three elevations in Sequoia NP and analyzed for eight pesticides by LeNoir et al. (1999). Air samples showed a decrease in pesticide concentration with elevation at the lower elevations. Pesticide residues found at highest concentration in Sequoia NP were generally those most heavily used in the Central Valley during summer: chlorpyrifos and endosulfan. Concentrations in surface waters decreased significantly above 2,040 m elevation. Pesticide concentrations were below acute toxicity values (LeNoir et al. 1999).

The Western Airborne Contaminant Assessment Project (WACAP) study measured inputs of airborne contaminants in a number of national parks in the western United States, including SEKI and YOSE, from 2002 to 2007. Along with Glacier (GLAC) and Rocky Mountain (ROMO) NPs, SEKI had some of the highest measured pesticide concentrations in many environmental compartments. All of these parks have relatively high regional agricultural development, which is the likely primary source of the observed contaminants (Landers et al. 2008). The semivolatile organic compounds (SOCs) detected in the air at SEKI by the WACAP study were mainly the CUPs endosulfan and dacthal. Except for polycyclic aromatic hydrocarbons (PAHs) and dacthal, all SOCs in air (hexachlorocyclohexane- γ , endosulfans, hexachlorocyclohexane- α , and chlordanes) at YOSE were above median values for WACAP parks.

Pesticide concentrations in SEKI and YOSE vegetation were among the highest measured by the WACAP study, along with vegetation in GLAC and Great Sand Dunes NP (Landers et al. 2008). Dominant SOC in SEKI vegetation included PAHs, endosulfans, dacthal, dichlorodiphenyltrichloroethane (DDT), chlorpyrifos, hexachlorobenzene, hexachlorocyclohexane- γ , dieldrin, hexachlorocyclohexane- α , and PCBs. In YOSE, dominant SOC in vegetation were the CUPs endosulfan and dacthal, followed by PAHs, chlorpyrifos, DDTs, and hexachlorobenzene. PCBs and selected pesticides (including chlorpyrifos and chlorothalonil) had previously been reported in brook trout and tree frogs (*Hyla regilla*) in the Kaweah River basin in Sequoia NP by Datta et al. (1998).

WACAP measurements of mercury (Hg) deposition fluxes to the snowpack were relatively low, consistent with the presence of few local or regional sources of Hg near SEKI. However, Hg concentrations in vegetation were comparatively high as compared with other WACAP parks, and fish were found that exceeded Hg health thresholds for wildlife and for humans (Landers et al. 2008). Krabbenhoft et al. (2002) sampled 90 lakes in seven of the WACAP national parks, including SEKI and YOSE, and analyzed their Hg and methylmercury (MeHg) concentrations. Levels of MeHg were lowest in GLAC (0.02 ng/L) and similar among all of the other parks (~ 0.05 ng/L).

Based on analyses conducted in WACAP, CUP concentrations were generally highest in fish collected from lakes in Sequoia NP, followed by ROMO and GLAC, and lowest in surveyed parks in the Pacific Northwest (Olympic and Mount Rainier NPs) and Alaska (Denali NP and Noatak National Preserve; Ackerman et al. 2008). DDT concentrations in several fish from Emerald and Pear Lakes in Sequoia NP exceeded health thresholds for kingfishers. These results suggest that organic contaminants deposited from the atmosphere onto remote national park watersheds in the western United States can accumulate in fish to levels that are of concern regarding wildlife health for some, but not all, wildlife species. Contaminant health thresholds for mink (*Mustela vison*) and river otter (*Lutra canadensis*), which are higher than those for kingfisher, were not exceeded by fish contaminant levels in any of the park lakes studied (Ackerman et al. 2008).

Simonich et al. (2012) reported SOC chemical burdens in ten salmonid fish taken from Mildred Lake in YOSE. Contaminant concentrations were generally similar to results from other studies in the Sierra Nevada, including in WACAP.

Cholinesterase (ChE) activity is a bioindicator of exposure to organophosphate pesticides (Ludke et al. 1975). Organophosphorus insecticides, such as malathion, chlorpyrifos, and diazinon, bind with ChE and interfere with neural function. Sparling et al. (2001) measured ChE activity and body residues in adult and tadpole life stages of Pacific treefrogs in California. ChE activity in tadpoles was lower in mountainous areas east of the Central Valley compared with habitats to the north or near the coast. ChE was also lower where ranid amphibian population status was poor or moderate. The frequency of detection and concentration of organophosphate pesticides in Pacific treefrog tissue followed north-south and west-east patterns that were consistent with agricultural sources of pesticides upwind of the areas having most severe amphibian decline. Reduced ChE activity in tadpoles has been shown to be associated with reduced activity, decreased growth, and increased mortality (Rosenbaum et al. 1988, Cowman and Mazanti 2000).

Fellers et al. (2004) measured pesticide concentrations in mountain yellow-legged frogs collected in the Sixty Lakes Basin in Kings Canyon NP and in the Tablelands area in Sequoia NP in 1997. The population in Kings Canyon NP appeared to be large and healthy; the Tablelands area once had a large population of this species, but it had been eliminated by the 1980s. Tablelands is exposed directly to the prevailing winds from agricultural areas located to the west. An experimental re-introduction of the frogs in 1994-1995 was not successful. The remaining 20 re-introduced frogs were captured and analyzed for tissue pesticide concentrations. Both γ -chlordane and trans-nonachlor were present at significantly higher concentration in the frogs collected from Tablelands as compared with Sixty Lakes Basin. The highest concentration of organochlorine pesticides was for DDE, which was 27 times higher, on average, in Tablelands (Fellers et al. 2004).

Fish were found in lakes in Sequoia NP with DDT concentrations that exceeded contaminant health thresholds for one or more piscivorous wildlife species. These concentrations exceeded levels detected in many fish collections around the world, even fish in Lake Malawi in East Africa, where DDT is sprayed as a mosquito control (Landers et al. 2010).

Fish from similar ecosystems in Canada had lower dieldrin concentrations as compared with fish from Sequoia NP. Both WACAP lakes in Sequoia NP had average dieldrin concentrations that exceeded human thresholds for subsistence fishers, and one fish exceeded the threshold for recreational human fishers (Landers et al. 2008).

A study was conducted of pesticide residues in brook trout and Pacific tree frogs in the Kaweah River watershed by Datta et al. (1998). Samples were collected along Sycamore Creek, at 610 m elevation, and compared with results for brook trout from Lake Tahoe and tree frog egg masses from Upper Meadows in Lassen Volcanic NP to the north of the SIEN. Concentrations of PCBs in brook trout taken from Sycamore Creek (4.8 to 8.1 ppb, wet weight) were similar to those found in lake trout in Lake Tahoe and rainbow trout in Marlette Lake. However, tree frog tadpoles and egg masses showed enriched levels of tri- and tetrachlorinated biphenyl congeners. Analyses for CUPs upwind from SEKI revealed the presence of chlorpyrifos, an organophosphate pesticide, and chlorothalnil, a chloronitrile fungicide. This may have implications for the observed decline in populations of some amphibian species in and around the SIEN national parks.

Ohyama et al. (2004) chose salmonid fish, mainly rainbow trout (*Oncorhynchus mykiss*), as an indicator to evaluate the transport and bioaccumulation of organochloride compounds in the northern and central Sierra Nevada. They found that elevation was an important factor affecting residual levels of PCBs in fish muscle tissue. On this basis, Ohyama et al. (2004) concluded that PCB residue in rainbow trout, a widely distributed salmonid species, provided a good monitoring tool for studying the effects of mountainous topography on the long-range transport and distribution of persistent organic pollutants.

Organochlorine chemicals can be estrogenic (Garcia-Reyero et al. 2007), contributing to the occurrence of intersex fish, and can accumulate in the aquatic food chains of remote mountain ecosystems (Blais et al. 1998). Biomarkers of exposure to estrogenic chemicals suggest the likelihood of reproductive dysfunction (Harries et al. 1997). Organochlorines are likely transported

as atmospheric contaminants to high-elevation sites (Hageman et al. 2006). Work by Schreck and Kent (2013) followed up on some of the work performed in the WACAP study. They expanded the range of coverage to additional western parks. The extent of endocrine disruption in fish was assessed in YOSE and SEKI within the SIEN. Of fish sampled in YOSE, one male brook trout was intersex. None of the fish sampled in SEKI (n=50 male fish) were intersex. The low observed frequency of intersex fish in study parks and water bodies in the SIEN may be a natural phenomenon (Schwindt et al. 2009). The extent to which human-caused contaminants contribute to an increased frequency is difficult to determine (Schreck and Kent 2013).

Wright et al. (2014) used surrogate artificial deposition surfaces, passive samplers, and temporal changes in Hg deposition and atmospheric concentrations to improve understanding of sources of Hg to remote western United States locations. Lowest Hg deposition (0.2 to 0.4 ng/m²/hr) occurred at low-elevation coastal sites. Highest deposition values (0.5 to 2.4 ng/m²/hr) were recorded in Great Basin National Park in the adjacent Mojave Desert Network and at a high-elevation (1279 m) coastal site. Intermediate deposition values were recorded at YOSE and SEKI (0.9 to 1.2 ng/m²/hr).

Hageman et al. (2010) reported results of pesticide analyses of snowpack at remote alpine, arctic, and subarctic sites in eight national parks, including SEKI. Various CUPs (dacthal, chlorpyrifos, endosulfans, and γ -hexachlorocyclohexane [HCH]) and historic use pesticides (HUPs; dieldrin, α -HCH, chlordanes, and hexachlorobenzene) were commonly measured at all sites and years (2003-2005). The pesticide concentration profiles were unique for individual parks, suggesting the importance of regional sources.

The distribution of CUPs among the parks were explained, using mass back trajectory analysis, based on the mass of individual CUPs used in regions located one-day upwind of the parks. For most pesticides and parks, more than 75% of the snowpack pesticide burden was attributed to regional transport. The authors concluded that the majority of pesticide contamination in U.S. national parks is due to regional pesticide applications.

Eagles-Smith et al. (2014) sampled fish in 21 national parks and analyzed them for Hg concentrations in tissue. Results varied substantially by park and by water body. Fish were sampled from four high-elevation lakes in SEKI. Concentrations of Hg in fish were generally low compared to other parks included in the study. Fish were analyzed for Hg in only two lakes in YOSE. At Spillway Lake, Hg concentrations were very low (mean 39 ng/g ww). In contrast, fish from Mildred Lake had much higher concentrations of fish Hg (mean 174 ng/g ww), and the levels in individual fish varied 15-fold. One fish had more than $1,100$ ng/g ww Hg. The cause(s) of this extreme variation is/are not known.

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NPS 963/132188, April 2016

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