National Park Service
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Natural Resource Stewardship and Science

Air Quality Related Values (AQRVs) in National Parks

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

Natural Resource Report NPS/ NRSS/ARD/NRR—2016/1196



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

Air Quality Related Values (AQRVs) in National Parks

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

Natural Resource Report NPS/ NRSS/ARD/NRR—2016/1196

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Abstract

A variety of air pollutants are emitted into the atmosphere from human-caused and natural emissions sources throughout the United States and elsewhere. These contaminants are transported with prevailing winds and impact sensitive natural resources in the national parks. This report provides a compilation and synthesis of current scientific understanding regarding the causes and effects of these pollutants within more than 270 Inventory and Monitoring national park lands throughout the United States. The pollutant categories of greatest concern and those that are evaluated here include ground-level ozone, which is not emitted directly from pollution sources, but rather is formed in the atmosphere in response to photochemical reactions that involve nitrogen oxides and volatile organic compounds. Other pollutants considered here include atmospheric particles that cause haze and degrade visibility and deposition from the atmosphere of acids (mainly sulfur, but also nitrogen), nutrients, and toxics. Emitted nutrients include oxidized and reduced forms of nitrogen. Toxics include mercury (a potent neurotoxin), a variety of historic and current-use pesticides, and other toxic materials. These contaminants are released into the air from such source types as power plants, motor vehicles, agriculture, industry, and others.

The level of adverse impact that occurs on national park resources in response to air pollution and pollutant deposition is governed primarily by the amount and types of pollutant exposure and by the inherent sensitivity of the park resources. Atmospheric deposition of acids, nutrients, and toxic materials varies considerably from park to park. Some parks receive quite substantial pollutant deposition loads; others are more remote from pollutant emissions sources and receive relatively low pollutant deposition loads. Vegetation in the parks is exposed to varying levels of atmospheric ozone that damages foliage. Varying levels of haze impair the ability of visitors to experience the scenic vistas offered by many of the parks.

Nevertheless, harm to park resources is not governed solely, or in many cases even mostly, by pollutant exposure. Parks also differ greatly in their inherent sensitivity to air pollution damage. Some park resources are highly sensitive to damage caused by inputs of acid precursors or nutrients. Some parks contain ecosystems that are highly sensitive to methylation that converts inorganic mercury to a form that can bioaccumulate to dangerously high levels in the food web. Some plant species are especially sensitive to foliar damage from exposure to atmospheric ozone. Some parks have outstanding visual resources such that even relatively low levels of haze dramatically affect visitor enjoyment of the park experience.

This report describes these pollutant emissions and deposition and the reasons for differences in resource sensitivity. Recent trends in pollutant exposure and adverse effects are highlighted. Mechanisms of impact are elucidated. Where possible, this report identifies the critical (tipping point) loads of pollutant deposition at which adverse impacts are manifested. Monitoring data are discussed along with mathematical model projections of future changes in resource conditions.

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Acronyms

Al	aluminum
Al^{3+}	free aluminum ion
Al_i	inorganic aluminum
$Al(OH)_3$	aluminum hydroxide
AMD	Acid mine drainage
ANC	acid neutralizing capacity
AOD	aerosol optical depth
AQRV	air quality related value
AQMS	Air Quality Management System
ARP	Acid Rain Program
As	arsenic
b_{ext}	light extinction coefficient
C	carbon
Ca	calcium
Ca^{2+}	calcium ion
CAA	Clean Air Act
CAAA	Amendments to the Clean Air Act
CAIR	Clean Air Interstate Rule
Cd	cadmium
CEC	cation exchange capacity
CENRAP	Central Regional Air Planning Association
CENTURY	model that simulates carbon, nitrogen, phosphorus, sulfur, and water dynamics in the soil-plant system at monthly intervals over time scales of centuries and millennia
CFCs	chlorinated fluorocarbons
CH_4	methane

CL	critical load
Cl	chlorine
Cl^-	chloride ion
CMAQ	Community Multiscale Air Quality (modeling system)
Co	cobalt
CO	carbon monoxide
CO_2	carbon dioxide
CONUS	continental U.S.
Cr	chromium
Cu	copper
CUP	current-use pesticide
DayCent	model for daily biogeochemistry for forest, grassland, cropland, and savanna systems
DDT	dichlorodiphenyltrichloroethane
DIC	dissolved inorganic carbon
DIN	dissolved inorganic nitrogen
DO	dissolved oxygen
DOC	dissolved organic carbon
DON	dissolved organic nitrogen
dv	deciview
EC	elemental carbon
EDC	endocrine disrupting compound
EGU	electricity generating unit
EPA	U.S. Environmental Protection Agency
EPT	Ephemeroptera-Plecoptera-Tricoptera (index)
ES	ecosystem services

F^-	fluorine ion
Fe	iron
F-factor	fraction of the change in mineral acid anions that is neutralized by base cation release
FHM	Forest Health Monitoring
FIA	Forest Inventory and Analysis (program)
FISH	Fish in Sensitive Habitats (project)
ForSAFE	three-component model of nitrogen, carbon cycling, and soil chemistry
FLAG	Federal Land Managers' Air Quality Related Values Work Group
FLM	Federal Land Manager
GEM	gaseous elemental Hg
GOM	gaseous oxidized Hg
H	hydrogen
H^+	proton, hydrogen ion
ha	hectare
HAP	hazardous air pollutant
HBEF	Hubbard Brook Experimental Forest
HCl	hydrochloric acid
HCO_3^-	bicarbonate
Hg	mercury
Hg^o	gaseous elemental mercury
Hg(II)	reactive Hg
$HgCl_2$	mercury chloride
HNO_3	nitric acid
HUC	hydrologic unit code
HUP	historic-use pesticide

I&M	Inventory and Monitoring
IA	Integrated Assessment
IMPROVE	Interagency Monitoring of Protected Visual Environments
ISA	Integrated Science Assessment
K	potassium
K^+	potassium ion
LIDAR	Light Detection and Ranging (remote sensing system)
LRTAP	Long Range Transport of Air Pollutants (program)
LTER	Long-Term Ecological Research (program)
LTM	Long-Term Monitoring (project)
MA	macrophage aggregate
MADPro	Mountain Acid Deposition Program
MAGIC	Model of Acidification of Groundwater in Catchments (model)
MANE-VU	Mid-Atlantic/Northeast Visibility Union
MDN	Mercury Deposition Network
MeHg	methylmercury
μeq	microequivalent
Mg	magnesium
Mg^{2+}	magnesium ion
MI	plant moisture availability index
mm	millimeters
Mn	manganese
N	nitrogen; population of resources
n	number of observations
N_2	nonreactive molecular nitrogen
NA	not available; insufficient data

Na	sodium
Na^+	sodium ion
NAAQS	National Ambient Air Quality Standards
NaCl	sodium chloride
NADP	National Atmospheric Deposition Program
NAPAP	National Acid Precipitation Assessment Program
NDDN	National Dry Deposition Network
NEI	National Emissions Inventory
NH_3	ammonia
NH_4^+	ammonium ion
NH_4NO_3	ammonium nitrate
$(NH_4)_2SO_4$	ammonium sulfate
NH_X	category label for NH_3 plus NH_4^+
Ni	nickel
NO_3^-	nitrate
NO_X	nitrogen oxides
NPS	National Park Service
N_r	reactive nitrogen
NTN	National Trends Network
O&G	oil and gas
O_3	ozone
P	phosphorus
PAHs	polycyclic aromatic hydrocarbons
PAN	peroxyacetyl nitrate
Pb	lead
PBDE	polybrominated diphenylether

PBM	particulate bound Hg
PCBs	polychlorinated biphenyl compounds
PCDD	polychlorinated dibenzo-p-dioxins
PCDF	polychlorinated dibenzofurans
PDSI	Palmer Drought Severity Index
pH	relative acidity
PM	particulate matter
$PM_{2.5}$	particulate matter with aerodynamic diameter smaller than 2.5 μm
PM_{10}	particulate matter with aerodynamic diameter smaller than 10 μm
POPs	persistent organic pollutants
ppb	parts per billion
ppbv	parts per billion by volume
p,p-DDE	dichlorodiphenyldichloroethylene
PSD	Prevention of Significant Deterioration
RH	relative humidity
RHR	regional haze rule
RPO	Regional Planning Organization
S	sulfur
SCP	spheroidal carbonaceous particles
Se	selenium
Si	silicon
SIP	State Implementation Plan
SO_2	sulfur dioxide
SO_4^{2-}	sulfate ion
SOC	semivolatile organic compound
SOS/T	State of Science/Technology (report)

SO_X	sulfur oxides
SUM06	seasonal sum of all hourly average O_3 concentrations ≥ 0.06 ppm
SWAS	Shenandoah Watershed Acidification Study
Ti	titanium
TL	target load
tpy	tons per year
UNEP	United Nations Environment Programme
USFS	U.S. Forest Service
USGS	U.S. Geological Survey
V	vanadium
V_d	deposition velocity
VISTAS	Visibility Improvement State and Tribal Association of the Southeast
VOC	volatile organic compound
VR	visual range
Vtg	vitellogenin
VTSSS	Virginia Trout Stream Sensitivity Study
W126	seasonal sum of hourly O_3 concentrations, with higher concentrations weighted more heavily
WACAP	Western Airborne Contaminants Assessment Project
WLS	Western Lakes Survey
WMP	Watershed Manipulation Project
WRAP	Western Regional Air Partnership
Zn	zinc

Introduction

One important goal of the National Park Service (NPS) is to protect park resources for the enjoyment of future generations. Unfortunately, however, many resources in the national parks are adversely impacted by a variety of forms of air pollution. Some air pollutants, called primary pollutants, are directly emitted into the atmosphere from various sources, including motor vehicles, power plants, industrial facilities, oil and gas (O&G) development, and agricultural activities. These primary pollutants are released into the environment from centers of human activities, including urban areas, agriculture, ground disturbance, and industrial development. Other air pollutants, called secondary pollutants, are formed in the atmosphere as a result of photochemical reactions. The various primary and secondary chemicals, particles, and gasses can be carried in the atmosphere short or long distances from their emissions source or atmospheric formation location and subsequently affect air quality related values (AQRVs) within the national parks.

Federal land managers (FLMs) have agreed (U.S. Forest Service et al. 2010) on the definition of an AQRV:

> *A resource, as identified by the FLM for one or more Federal areas, that may be adversely affected by a change in air quality. The resource may include visibility or a specific scenic, cultural, physical, biological, ecological, or recreational resource identified by the FLM for a particular area.*

These AQRVs can include aspects of visibility, water quality, and the health and vitality of plants, animals, and other life forms that reside in and around the national park lands. Some of the same air pollutants that can adversely affect visibility and the health and vitality of natural resources can also affect stonework and other cultural resources. Both wet, and especially dry, deposition of acids contribute to erosion of buildings, monuments, statues, ancient ruins, and other valued structures. Particles that cause regional haze also contribute to pitting of stonework. The NPS National Center for Preservation Technology and Training has studied impacts of air pollution on cultural resources (http://ncptt.nps.gov/). The remainder of this document will focus primarily on air pollution and its effects on visibility and natural resources, with little additional mention of effects on cultural resources.

Visitors to the national parks expect clean, clear air, healthy plants, and abundant wildlife. Visitors enjoy and remember breathtaking scenes of mountains, valleys, and shorelines, and the forms and textures of unique landscapes. Enjoyment and appreciation of AQRVs are integral parts of the visitor experience. The quality of the experience is inextricably linked to the visitor's ability to view the parks unobstructed by haze and the knowledge that park ecosystems are healthy and will remain so for future generations.

Background and Purpose

Long-term monitoring and short-term research projects in the national parks have shown that human-caused air pollution has adversely impacted air quality, visibility, streamwater chemistry, soil condition, and native biota in some parks. Despite recent improvements in air quality under the Clean Air Act (CAA) and its amendments, the visibility and sensitive aquatic and terrestrial systems in some parks are still adversely impacted relative to estimated natural or pre-industrial background conditions; because of their high degree of sensitivity, they will likely remain at risk after full implementation of the 1990 CAA Amendments (CAAA).

Ecosystem effects from air pollution in some of the national parks have been substantial. Efforts to characterize and quantify these impacts, and to examine more recent recovery as some air pollution levels decline in some areas, have focused primarily on visibility, surface waters, soils, and forests. Although visibility is still considered degraded in many parks, impairing visitor enjoyment of scenic vistas, conditions have generally improved in recent years. As sulfur (S), nitrogen (N), and mercury (Hg) emissions continue to be controlled, some surface waters and soils show signs of partial chemical recovery (Lawrence et al. 2011, Lawrence et al. 2012). Nevertheless, available data suggest that soil chemistry will continue to deteriorate in some regions under expected future emissions and deposition (Warby et al. 2009), and these changes in soil condition may continue to affect future lake and stream water chemistry (Sullivan et al. 2006). Biological dose-response functions for some sensitive receptors have been developed (Cosby et al. 2006, Sullivan et al. 2006, Sullivan et al. 2013). These data inform the calculation of chemical and ecosystem indicator variables for defining critical loads (CL)[1] and recovery targets. Chemical and biological responses to decreases in deposition are being quantified at some monitoring sites as air pollution and atmospheric deposition continue to decline. Resource managers, policymakers, and scientists now need to know the status of terrestrial and aquatic receptors, the existing level of damage to sensitive receptors, the extent to which current and projected future emissions reductions will lead to ecosystem recovery (both chemical and biological), the deposition levels that will be required to promote recovery, and the ways in which biogeochemical processes govern elemental cycles and ecosystem responses to atmospheric deposition and other forms of air pollution. Synthesis and integration of existing data and knowledge and assembly of sensitive receptor inventories will provide a stronger basis for setting further emissions reduction goals, evaluating incremental improvements, conducting cost/benefit analyses, and prioritizing research and monitoring needs in the national parks.

This report synthesizes available inventories and published findings regarding AQRVs sensitive to impacts due to the atmospheric deposition of N, S, and toxic compounds, formation of ground-level ozone (O_3), and impacts on in-park visibility. Chapter 1 of this report provides background

[1] A critical load of atmospheric deposition is the level of deposition below which adverse effects do not occur according to current knowledge.

information on emissions, deposition, and effects of air pollutants. It is followed by 32 individual reports with network-specific and park-specific AQRV information.

There is a growing body of scientific research demonstrating that atmospheric deposition and other aspects of air pollution induce a range of effects on aquatic and terrestrial ecosystems and visual resources from subtle to severe. Such effects include those associated with acidification, nutrient enrichment, visibility impairment, and toxicity. The Natural Resource Challenge Action Plan (NPS 1999) outlines a strategy to improve the scientific basis for how the NPS manages natural resources under its care. A major component of the strategy includes development of comprehensive inventories of natural resources in parks, including air quality and AQRVs. This report summarizes information from the AQRV inventories.

Through the Federal Land Managers' Air Quality Related Values Work Group (FLAG) Phase I report (U.S. Forest Service et al. 2000, 2010), the FLMs have made progress towards agreeing on the levels of air pollution that trigger concerns for AQRVs. Nevertheless, difficulties arise in assessing the impacts of multiple sources simultaneously, whereby a large number of minor sources can collectively contribute to an unacceptable cumulative impact, or when a new potential emissions source applies for a Prevention of Significant Deterioration (PSD) permit in an area that already has a high level of air pollution from existing emissions sources.

The NPS has a fundamental legislative mandate to protect park resources, including AQRVs, from the adverse effects of air pollution so as to leave them unimpaired for the enjoyment of future generations (Shaver et al. 1994). NPS Management Policies (2006) state that

> *The Service will actively promote and pursue measures to protect these values from the adverse impacts of air pollution. In cases of doubt as to the impacts of existing or potential air pollution on park resources, the Service will err on the side of protecting air quality and related values for future generations*.

This report provides NPS with critical information needed to comply with that mandate.

In addition, Congress assigned to the FLMs a responsibility to protect AQRVs in Federal Class I areas[2], which are afforded the highest level of protection under the CAA. This includes identifying AQRVs in each Class I area, establishing and prioritizing inventory and monitoring protocols, specifying a process for evaluation of air pollution effects on AQRVs, and specifying adverse effects on each AQRV. An adverse effect is one that diminishes the Class I area's significance, impairs the structure or function of the protected ecosystem, and/or impairs the quality of the visitor experience.

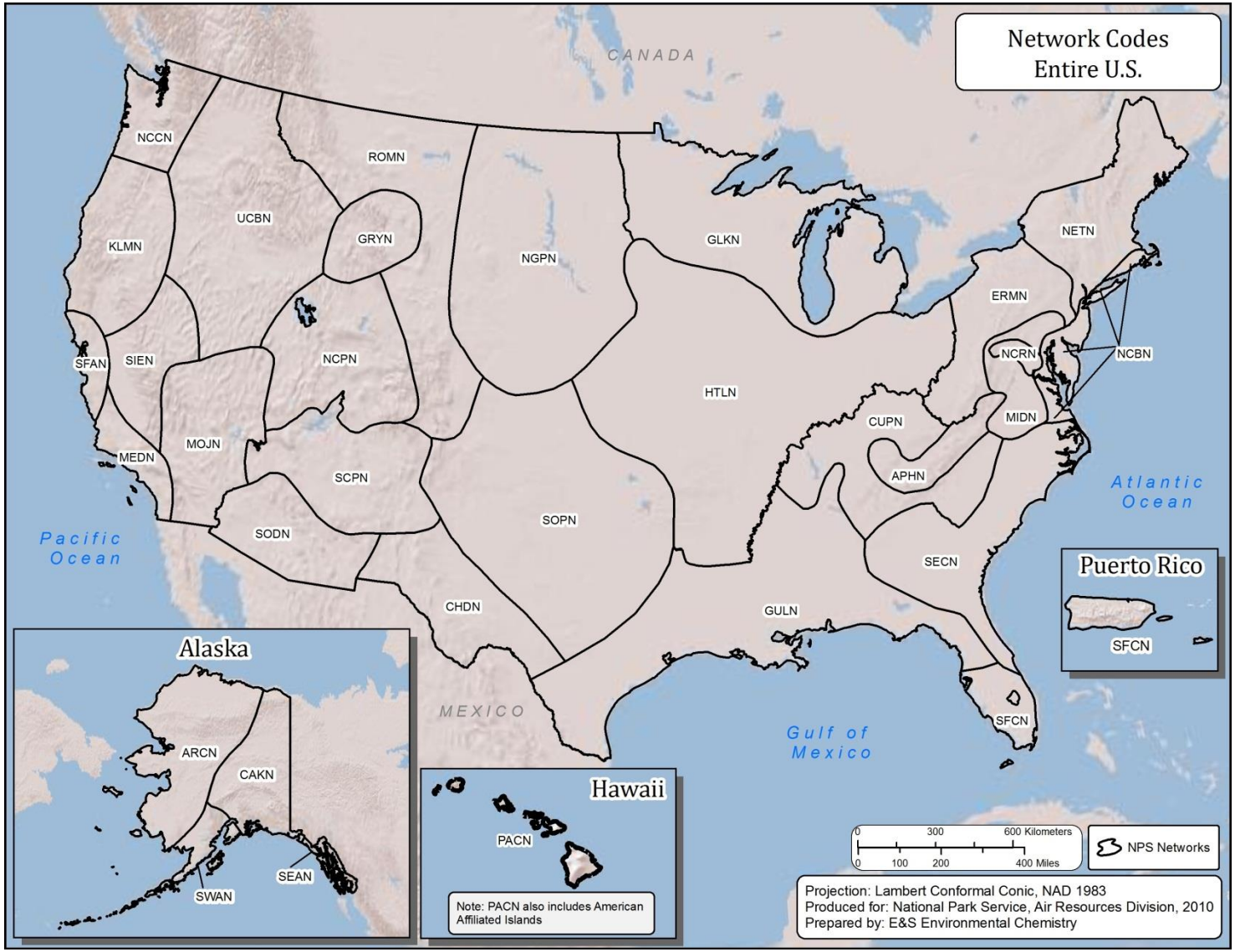
Over the past several decades, various parks within the NPS system have been subjects of a wide variety of air pollution effects characterization and monitoring studies, including:

[2] Class I areas include certain national park and wilderness areas, of a certain minimum size and establishment date

- wet deposition monitoring
- dry deposition monitoring
- ground-level O_3 monitoring
- visibility optical monitoring (light extinction and light scattering)
- visibility particle monitoring
- photographic visibility monitoring (including webcams)
- ozone precursor (nitrogen oxides [NO_x] and volatile organic compounds [VOCs]) studies
- streamwater chemistry
- soil chemistry
- nutrient cycling
- ecosystem and atmospheric modeling
- effects on fish and other aquatic and terrestrial biota
- effects on vegetation and lichens

Key information from these studies was compiled for this assessment along with results from various regional and national studies. Much of the information was developed for the NPS Inventory and Monitoring Program, which organizes the approximately 270 parks containing significant natural resources into 32 networks. The principal objective of this report is to synthesize and assess available information on AQRVs in I&M national parks throughout the United States. The current status of air pollution-sensitive resources was evaluated, along with available dynamic, steady-state, and empirical model simulations of CL and future prognosis for damage or recovery. Data were gathered for individual parks where available. Park-specific analyses focused primarily on those parks thought to contain the greatest concentration of air pollution-sensitive resources and those parks that have been most intensively studied. These tend to be the larger parks.

Locations of the NPS I&M networks that provide the organization for this assessment are shown in Map 1. The I&M parks and networks are listed in Tables 1 and 2. These national-level data provide context for comparing exposures and sensitivities across parks and networks. In Section 2 of this report, site-specific research results provide an indication of the status of the AQRVs in I&M parks in each network across the nation. The data layers that provided the foundation for assessing the broad spatial patterns for each air pollution stressor are described below.



Map 1. Locations of I&M networks. The network names associated with the four-letter identification codes are given in Table 1.

Table 1. List of Inventory and Monitoring networks and associated network codes.

Network Name	Network Code
Appalachian Highlands	APHN
Arctic	ARCN
Central Alaska	CAKN
Chihuahuan Desert	CHDN
Cumberland Piedmont	CUPN
Eastern Rivers and Mountains	ERMN
Great Lakes	GLKN
Greater Yellowstone	GRYN
Gulf Coast	GULN
Heartland	HTLN
Klamath	KLMN
Mediterranean Coast	MEDN
Mid Atlantic	MIDN
Mojave Desert	MOJN
National Capital Region	NCRN
North Coast and Cascades	NCCN
Northeast Coastal and Barrier	NCBN
Northeast Temperate	NETN
Northern Colorado Plateau	NCPN
Northern Great Plains	NGPN
Pacific Island	PACN
Rocky Mountain	ROMN
San Francisco Bay Area	SFAN
Sierra Nevada	SIEN
Sonoran Desert	SODN
South Florida Caribbean	SFCN
Southeast Alaska	SEAN
Southeast Coast	SECN
Southern Colorado Plateau	SCPN
Southern Plains	SOPN
Southwest Alaska	SWAN
Upper Columbia Basin	UCBN

Table 2. List of national park lands and associated codes.

Park Name	Park Code	Network Name	Network Code
Abraham Lincoln Birthplace	ABLI	Cumberland Piedmont	CUPN
Acadia	ACAD	Northeast Temperate	NETN
Agate Fossil Beds	AGFO	Northern Great Plains	NGPN
Alagnak	ALAG	Southwest Alaska	SWAN
Alibates Flint Quarries	ALFL	Southern Plains	SOPN
Allegheny Portage Railroad	ALPO	Eastern Rivers and Mountains	ERMN
American Memorial Park	AMME	Pacific Island	PACN
Amistad	AMIS	Chihuahuan Desert	CHDN
Aniakchak	ANIA	Southwest Alaska	SWAN
Antietam	ANTI	National Capital Region	NCRN
Apostle Islands	APIS	Great Lakes	GLKN
Appomattox Court House	APCO	Mid Atlantic	MIDN
Arches	ARCH	Northern Colorado Plateau	NCPN
Arkansas Post	ARPO	Heartland	HTLN
Assateague Island	ASIS	Northeast Coastal and Barrier	NCBN
Aztec Ruins	AZRU	Southern Colorado Plateau	SCPN
Badlands	BADL	Northern Great Plains	NGPN
Bandelier	BAND	Southern Colorado Plateau	SCPN
Bent's Old Fort	BEOL	Southern Plains	SOPN
Bering Land Bridge	BELA	Arctic	ARCN
Big Bend	BIBE	Chihuahuan Desert	CHDN
Big Cypress	BICY	South Florida_Caribbean	SFCN
Big Hole	BIHO	Upper Columbia Basin	UCBN
Big South Fork	BISO	Appalachian Highlands	APHN
Big Thicket	BITH	Gulf Coast	GULN
Bighorn Canyon	BICA	Greater Yellowstone	GRYN
Biscayne	BISC	South Florida_Caribbean	SFCN
Black Canyon of the Gunnison	BLCA	Northern Colorado Plateau	NCPN
Blue Ridge	BLRI	Appalachian Highlands	APHN
Bluestone	BLUE	Eastern Rivers and Mountains	ERMN
Booker T. Washington	BOWA	Mid Atlantic	MIDN
Boston Harbor Islands	BOHA	Northeast Temperate	NETN
Bryce Canyon	BRCA	Northern Colorado Plateau	NCPN
Buck Island Reef	BUIS	South Florida_Caribbean	SFCN
Buffalo	BUFF	Heartland	HTLN

Table 2 (continued). List of national park lands and associated codes.

Park Name	Park Code	Network Name	Network Code
Cabrillo	CABR	Mediterranean Coast	MEDN
Canaveral	CANA	Southeast Coast	SECN
Canyon de Chelly	CACH	Southern Colorado Plateau	SCPN
Canyonlands	CANY	Northern Colorado Plateau	NCPN
Cape Cod	CACO	Northeast Coastal and Barrier	NCBN
Cape Hatteras	CAHA	Southeast Coast	SECN
Cape Krusenstern	CAKR	Arctic	ARCN
Cape Lookout	CALO	Southeast Coast	SECN
Capitol Reef	CARE	Northern Colorado Plateau	NCPN
Capulin Volcano	CAVO	Southern Plains	SOPN
Carl Sandburg Home	CARL	Cumberland_Piedmont	CUPN
Carlsbad Caverns	CAVE	Chihuahuan Desert	CHDN
Casa Grande Ruins	CAGR	Sonoran Desert	SODN
Castillo de San Marcos	CASA	Southeast Coast	SECN
Catoctin Mountain	CATO	National Capital Region	NCRN
Cedar Breaks	CEBR	Northern Colorado Plateau	NCPN
Chaco Culture	CHCU	Southern Colorado Plateau	SCPN
Channel Islands	CHIS	Mediterranean Coast	MEDN
Chattahoochee River	CHAT	Southeast Coast	SECN
Chesapeake and Ohio Canal	CHOH	National Capital Region	NCRN
Chickamauga and Chattanooga	CHCH	Cumberland_Piedmont	CUPN
Chickasaw	CHIC	Southern Plains	SOPN
Chiricahua	CHIR	Sonoran Desert	SODN
City of Rocks	CIRO	Upper Columbia Basin	UCBN
Colonial	COLO	Northeast Coastal and Barrier	NCBN
Colorado	COLM	Northern Colorado Plateau	NCPN
Congaree	COSW	Southeast Coast	SECN
Coronado	CORO	Sonoran Desert	SODN
Cowpens	COWP	Cumberland_Piedmont	CUPN
Crater Lake	CRLA	Klamath	KLMN
Craters of the Moon	CRMO	Upper Columbia Basin	UCBN
Cumberland Gap	CUGA	Cumberland_Piedmont	CUPN
Cumberland Island	CUIS	Southeast Coast	SECN
Curecanti	CURE	Northern Colorado Plateau	NCPN
Cuyahoga Valley	CUVA	Heartland	HTLN

Table 2 (continued). List of national park lands and associated codes.

Park Name	Park Code	Network Name	Network Code
Death Valley	DEVA	Mojave Desert	MOJN
Delaware Water Gap	DEWA	Eastern Rivers and Mountains	ERMN
Denali	DENA	Central Alaska	CAKN
Devils Postpile	DEPO	Sierra Nevada	SIEN
Devils Tower	DETO	Northern Great Plains	NGPN
Dinosaur	DINO	Northern Colorado Plateau	NCPN
Dry Tortugas	DRTO	South Florida_Caribbean	SFCN
Ebey's Landing	EBLA	North Coast and Cascades	NCCN
Effigy Mounds	EFMO	Heartland	HTLN
Eisenhower	EISE	Mid Atlantic	MIDN
El Malpais	ELMA	Southern Colorado Plateau	SCPN
El Morro	ELMO	Southern Colorado Plateau	SCPN
Everglades	EVER	South Florida_Caribbean	SFCN
Fire Island	FIIS	Northeast Coastal and Barrier	NCBN
Florissant Fossil Beds	FLFO	Rocky Mountain	ROMN
Fort Bowie	FOBO	Sonoran Desert	SODN
Fort Caroline	FOCA	Southeast Coast	SECN
Fort Davis	FODA	Chihuahuan Desert	CHDN
Fort Donelson	FODO	Cumberland_Piedmont	CUPN
Fort Frederica	FOFR	Southeast Coast	SECN
Fort Laramie	FOLA	Northern Great Plains	NGPN
Fort Larned	FOLS	Southern Plains	SOPN
Fort Matanzas	FOMA	Southeast Coast	SECN
Fort Necessity	FONE	Eastern Rivers and Mountains	ERMN
Fort Point	FOPO	San Francisco Bay Area	SFAN
Fort Pulaski	FOPU	Southeast Coast	SECN
Fort Sumter	FOSU	Southeast Coast	SECN
Fort Union	FOUN	Southern Plains	SOPN
Fort Union Trading Post	FOUS	Northern Great Plains	NGPN
Fort Vancouver	FOVA	North Coast and Cascades	NCCN
Fossil Butte	FOBU	Northern Colorado Plateau	NCPN
Fredericksburg and Spotsylvania	FRSP	Mid Atlantic	MIDN
Friendship Hill	FRHI	Eastern Rivers and Mountains	ERMN
Gates of the Arctic	GAAR	Arctic	ARCN
Gateway	GATE	Northeast Coastal and Barrier	NCBN

Table 2 (continued). List of national park lands and associated codes.

Park Name	Park Code	Network Name	Network Code
Gauley River	GARI	Eastern Rivers and Mountains	ERMN
George Washington	GWMP	National Capital Region	NCRN
George Washington Birthplace	GEWA	Northeast Coastal and Barrier	NCBN
George Washington Carver	GWCA	Heartland	HTLN
Gettysburg	GETT	Mid Atlantic	MIDN
Gila Cliff Dwellings	GICL	Sonoran Desert	SODN
Glacier	GLAC	Rocky Mountain	ROMN
Glacier Bay	GLBA	Southeast Alaska	SEAN
Glen Canyon	GLCA	Southern Colorado Plateau	SCPN
Golden Gate	GOGA	San Francisco Bay Area	SFAN
Golden Spike	GOSP	Northern Colorado Plateau	NCPN
Grand Canyon	GRCA	Southern Colorado Plateau	SCPN
Grand Portage	GRPO	Great Lakes	GLKN
Grand Teton	GRTE	Greater Yellowstone	GRYN
Grant-Kohrs Ranch	GRKO	Rocky Mountain	ROMN
Great Basin	GRBA	Mojave Desert	MOJN
Great Sand Dunes	GRSA	Rocky Mountain	ROMN
Great Smoky Mountains	GRSM	Appalachian Highlands	APHN
Guadalupe Mountains	GUMO	Chihuahuan Desert	CHDN
Guilford Courthouse	GUCO	Cumberland_Piedmont	CUPN
Gulf Islands	GUIS	Gulf Coast	GULN
Hagerman Fossil Beds	HAFO	Upper Columbia Basin	UCBN
Haleakala	HALE	Pacific Island	PACN
Harpers Ferry	HAFE	National Capital Region	NCRN
Hawaii Volcanoes	HAVO	Pacific Island	PACN
Herbert Hoover	HEHO	Heartland	HTLN
Home of Franklin D. Roosevelt	HOFR	Northeast Temperate	NETN
Homestead	HOME	Heartland	HTLN
Hopewell Culture	HOCU	Heartland	HTLN
Hopewell Furnace	HOFU	Mid Atlantic	MIDN
Horseshoe Bend	HOBE	Southeast Coast	SECN
Hot Springs	HOSP	Heartland	HTLN
Hovenweep	HOVE	Northern Colorado Plateau	NCPN
Hubbell Trading Post	HUTR	Southern Colorado Plateau	SCPN
Indiana Dunes	INDU	Great Lakes	GLKN

Table 2 (continued). List of national park lands and associated codes.

Park Name	Park Code	Network Name	Network Code
Isle Royale	ISRO	Great Lakes	GLKN
Jean Lafitte	JELA	Gulf Coast	GULN
Jewel Cave	JECA	Northern Great Plains	NGPN
John Day Fossil Beds	JODA	Upper Columbia Basin	UCBN
John Muir	JOMU	San Francisco Bay Area	SFAN
Johnstown Flood	JOFL	Eastern Rivers and Mountains	ERMN
Joshua Tree	JOTR	Mojave Desert	MOJN
Kalaupapa	KALA	Pacific Island	PACN
Kaloko-Honokohau	KAHO	Pacific Island	PACN
Katmai	KATM	Southwest Alaska	SWAN
Kenai Fjords	KEFJ	Southwest Alaska	SWAN
Kennesaw Mountain	KEMO	Southeast Coast	SECN
Kings Canyon	KICA	Sierra Nevada	SIEN
Kings Mountain	KIMO	Cumberland_Piedmont	CUPN
Klondike Gold Rush	KLGO	Southeast Alaska	SEAN
Knife River Indian Villages	KNRI	Northern Great Plains	NGPN
Kobuk Valley	KOVA	Arctic	ARCN
Lake Clark	LACL	Southwest Alaska	SWAN
Lake Mead	LAME	Mojave Desert	MOJN
Lake Meredith	LAMR	Southern Plains	SOPN
Lake Roosevelt	LARO	Upper Columbia Basin	UCBN
Lassen Volcanic	LAVO	Klamath	KLMN
Lava Beds	LABE	Klamath	KLMN
Lewis and Clark	LEWI	North Coast and Cascades	NCCN
Lincoln Boyhood	LIBO	Heartland	HTLN
Little Bighorn Battlefield	LIBI	Rocky Mountain	ROMN
Little River Canyon	LIRI	Cumberland_Piedmont	CUPN
Lyndon B. Johnson	LYJO	Southern Plains	SOPN
Mammoth Cave	MACA	Cumberland_Piedmont	CUPN
Manassas	MANA	National Capital Region	NCRN
Manzanar	MANZ	Mojave Desert	MOJN
Marsh-Billings-Rockefeller	MABI	Northeast Temperate	NETN
Mesa Verde	MEVE	Southern Colorado Plateau	SCPN
Minute Man	MIMA	Northeast Temperate	NETN
Mississippi	MISS	Great Lakes	GLKN

Table 2 (continued). List of national park lands and associated codes.

Park Name	Park Code	Network Name	Network Code
Missouri	MNRR	Northern Great Plains	NGPN
Mojave	MOJA	Mojave Desert	MOJN
Monocacy	MONO	National Capital Region	NCRN
Montezuma Castle	MOCA	Sonoran Desert	SODN
Moores Creek	MOCR	Southeast Coast	SECN
Morristown	MORR	Northeast Temperate	NETN
Mount Rainier	MORA	North Coast and Cascades	NCCN
Mount Rushmore	MORU	Northern Great Plains	NGPN
Muir Woods	MUWO	San Francisco Bay Area	SFAN
Natchez Trace Parkway and National Scenic Trail	NATR	Gulf Coast	GULN
National Capital Parks - East	NACE	National Capital Region	NCRN
National Park of American Samoa	NPSA	Pacific Island	PACN
Natural Bridges	NABR	Northern Colorado Plateau	NCPN
Navajo	NAVA	Southern Colorado Plateau	SCPN
New River Gorge	NERI	Eastern Rivers and Mountains	ERMN
Nez Perce	NEPE	Upper Columbia Basin	UCBN
Ninety Six	NISI	Cumberland_Piedmont	CUPN
Niobrara	NIOB	Northern Great Plains	NGPN
Noatak	NOAT	Arctic	ARCN
North Cascades	NOCA	North Coast and Cascades	NCCN
Obed	OBRI	Appalachian Highlands	APHN
Ocmulgee	OCMU	Southeast Coast	SECN
Olympic	OLYM	North Coast and Cascades	NCCN
Oregon Caves	ORCA	Klamath	KLMN
Organ Pipe Cactus	ORPI	Sonoran Desert	SODN
Ozark	OZAR	Heartland	HTLN
Padre Island	PAIS	Gulf Coast	GULN
Palo Alto Battlefield	PAAL	Gulf Coast	GULN
Pea Ridge	PERI	Heartland	HTLN
Pecos	PECO	Southern Plains	SOPN
Petersburg	PETE	Mid Atlantic	MIDN
Petrified Forest	PEFO	Southern Colorado Plateau	SCPN
Petroglyph	PETR	Southern Colorado Plateau	SCPN
Pictured Rocks	PIRO	Great Lakes	GLKN

Table 2 (continued). List of national park lands and associated codes.

Park Name	Park Code	Network Name	Network Code
Pinnacles	PINN	San Francisco Bay Area	SFAN
Pipe Spring	PISP	Northern Colorado Plateau	NCPN
Pipestone	PIPE	Heartland	HTLN
Point Reyes	PORE	San Francisco Bay Area	SFAN
Prince William Forest	PRWI	National Capital Region	NCRN
Pu'uhonua o Honaunau	PUHO	Pacific Island	PACN
Puukohola Heiau	PUHE	Pacific Island	PACN
Rainbow Bridge	RABR	Southern Colorado Plateau	SCPN
Redwood	REDW	Klamath	KLMN
Richmond	RICH	Mid Atlantic	MIDN
Rock Creek Park	ROCR	National Capital Region	NCRN
Rocky Mountain	ROMO	Rocky Mountain	ROMN
Russell Cave	RUCA	Cumberland_Piedmont	CUPN
Sagamore Hill	SAHI	Northeast Coastal and Barrier	NCBN
Saguaro	SAGU	Sonoran Desert	SODN
Saint Croix	SACN	Great Lakes	GLKN
Saint-Gaudens	SAGA	Northeast Temperate	NETN
Salinas Pueblo Missions	SAPU	Southern Colorado Plateau	SCPN
San Antonio Missions	SAAN	Gulf Coast	GULN
San Juan Island	SAJH	North Coast and Cascades	NCCN
Santa Monica Mountains	SAMO	Mediterranean Coast	MEDN
Saratoga	SARA	Northeast Temperate	NETN
Saugus Iron Works	SAIR	Northeast Temperate	NETN
Scotts Bluff	SCBL	Northern Great Plains	NGPN
Sequoia	SEQU	Sierra Nevada	SIEN
Shenandoah	SHEN	Mid Atlantic	MIDN
Shiloh	SHIL	Cumberland_Piedmont	CUPN
Sitka	SITK	Southeast Alaska	SEAN
Sleeping Bear Dunes	SLBE	Great Lakes	GLKN
Stones River	STRI	Cumberland_Piedmont	CUPN
Sunset Crater Volcano	SUCR	Southern Colorado Plateau	SCPN
Tallgrass Prairie	TAPR	Heartland	HTLN
Theodore Roosevelt	THRO	Northern Great Plains	NGPN
Thomas Stone	THST	Northeast Coastal and Barrier	NCBN

Table 2 (continued). List of national park lands and associated codes.

Park Name	Park Code	Network Name	Network Code
Timpanogos Cave	TICA	Northern Colorado Plateau	NCPN
Timucaun Ecological and Historical Preserve	TIMU	Southeast Coast	SECN
Tonto	TONT	Sonoran Desert	SODN
Tumacacori	TUMA	Sonoran Desert	SODN
Tuzigoot	TUZI	Sonoran Desert	SODN
Upper Delaware	UPDE	Eastern Rivers and Mountains	ERMN
Valley Forge	VAFO	Mid Atlantic	MIDN
Vanderbilt Mansion	VAMA	Northeast Temperate	NETN
Vicksburg	VICK	Gulf Coast	GULN
Virgin Islands	VIIS	South Florida/Caribbean	SFCN
Voyageurs	VOYA	Great Lakes	GLKN
Walnut Canyon	WACA	Southern Colorado Plateau	SCPN
War in the Pacific	WAPA	Pacific Island	PACN
Washita Battlefield	WABA	Southern Plains	SOPN
Weir Farm	WEFA	Northeast Temperate	NETN
Whiskeytown	WHIS	Klamath	KLMN
White Sands	WHSA	Chihuahuan Desert	CHDN
Whitman Mission	WHMI	Upper Columbia Basin	UCBN
Wilson's Creek	WICR	Heartland	HTLN
Wind Cave	WICA	Northern Great Plains	NGPN
Wolf Trap National Park for the Performing Arts	WOTR	National Capital Region	NCRN
Wrangell-St. Elias	WRST	Central Alaska	CAKN
Wupatki	WUPA	Southern Colorado Plateau	SCPN
Yellowstone	YELL	Greater Yellowstone	GRYN
Yosemite	YOSE	Sierra Nevada	SIEN
Yucca House	YUHO	Southern Colorado Plateau	SCPN
Yukon-Charley Rivers	YUCH	Central Alaska	CAKN
Zion	ZION	Northern Colorado Plateau	NCPN

Emissions and Atmospheric Deposition

Emissions

Emissions into the atmosphere of a wide range of substances can impact sensitive resources in national parks at down-wind locations. The air pollutants of concern for this report regarding air pollution impacts include gases and particles containing S, N, Hg and other metals, pesticides and other organic compounds, O_3, and particles that obscure visibility. Emissions sources are varied, and in particular include power plants, industrial facilities, motor vehicles, incinerators, agriculture, fire, O&G development, and other human-caused and natural sources. Air pollutants can cause or contribute to numerous adverse impacts. These include acidification of soil and water; eutrophication of terrestrial and aquatic ecosystems; biomagnification and toxicity of contaminants; inhibition of plant health, growth or reproduction; changes in species composition and abundance; and visibility degradation.

Human-caused emissions of S, N, and Hg have decreased over the past decade or more throughout much of the United States in response to emissions controls, particularly controls on large power plants and vehicles. In general, the states that have had the highest levels of S and N emissions have shown the largest reductions in response to Acid Rain Program (ARP) regulations (Burns et al. 2011). However, in some regions, increasing emissions from O&G production, agriculture, and other sources may offset the reductions achieved by ARP and other air quality improvement programs. Changes in climate can also have profound effects on air quality and air pollution impacts.

Jacob and Winner (2009) provide a comprehensive review. For example, dramatic heat waves in the eastern United States (1988) and Europe (2003) were accompanied by major air pollution episodes (Guerova and Jones 2007, Lin et al. 2001). Under a warming climate, major heat waves are expected to become more common (Christensen et al. 2007). Ozone concentrations in atmospheric surface layers are correlated with air temperature (Jacob and Winner 2009). There may be multiple causes of this relationship, including associations among high temperature, high O_3, and air stagnation. In addition, O_3 formation is partly dependent on biogenic isoprene emissions from vegetation, which are temperature dependent (Jacob et al. 1993, Jacob et al. 2011).

Increased atmospheric carbon dioxide (CO_2), warming temperatures, and altered hydrologic regimes associated with climate change modify specific effects of air pollutants and influence sensitive ecosystem acid-base chemistry, nutrient cycling, O_3 exposure, and visibility degradation. In addition, many prominent air pollutants, including CO_2, methane (CH_4), S, and particulate matter (PM), are important climate forcing agents. Thus, it is important to consider air pollution from a global holistic perspective and to more effectively integrate goals focused collectively on land use, air quality, and climate in setting environmental policy (Jacob et al. 2011)Previous national-scale air pollution sensitivity and effects screening assessments conducted for the National Park Service Air Resources Division (NPS-ARD; Sullivan et al. 2011a, Sullivan et al. 2011b) relied upon emissions and deposition data for the period 2001-2003, as these were the most current data available at the time of preparation of those assessments. Since that time, emissions in proximity to national park lands and deposition within park borders have changed. At many locations, especially in the eastern United

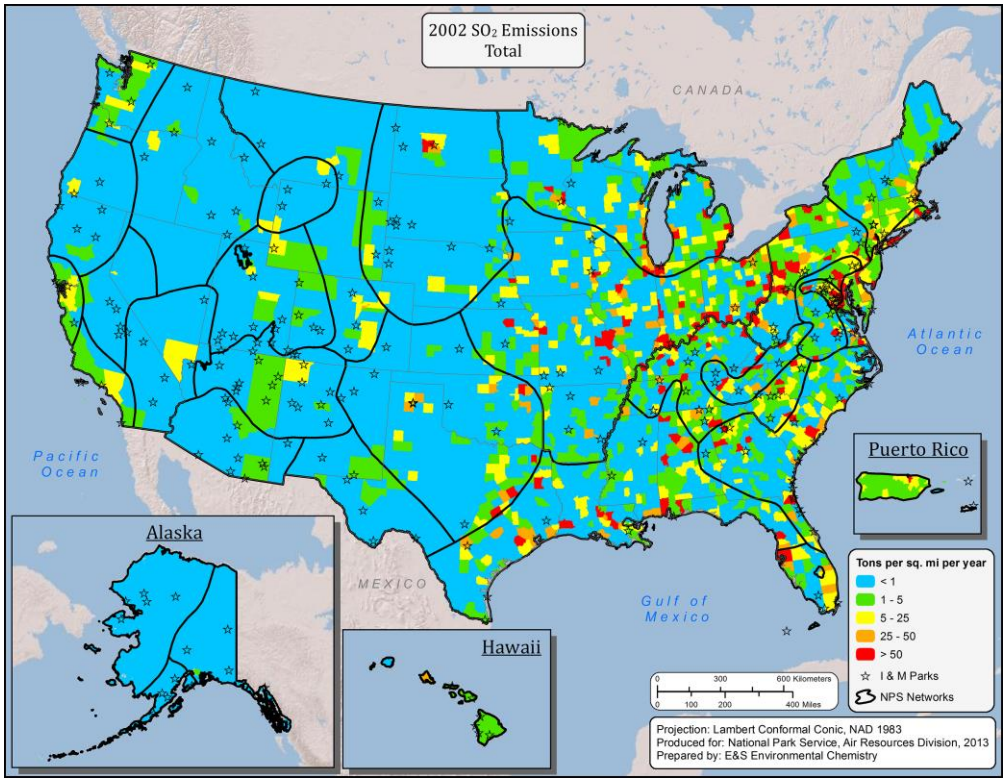
States, S and oxidized N emissions and deposition levels have decreased, in large part due to legislated emissions controls on coal-fired power plants and other major pollutant sources (Haeuber 2013). Emissions and deposition of reduced N (NH_3, NH_4^+) have more commonly increased. Emissions were expressed by Sullivan et al. (2011a, 2011b) as annual estimates; deposition was expressed as three-year annual averages to account for variation in weather conditions. These estimates are updated here by calculating analogous estimates focused on the year 2011. Emissions estimates for S and N were obtained from the Environmental Protection Agency's National Emissions Inventory (NEI) for 2011.

The largest sources of sulfur dioxide (SO_2) emissions in the United States are coal-fired power plants, as coal contains varying amounts of S. Historically, the states having the largest SO_2 emissions have included Illinois, Indiana, Kentucky, Missouri, Ohio, Pennsylvania, Tennessee, and West Virginia. These states lie upwind of extensive national park and wilderness areas that are sensitive to the acidifying effects of S. There are also large SO_2 emissions sources scattered elsewhere throughout the country, and many of them are in proximity to national parks. The ARP required substantial reductions in the atmospheric emissions of SO_2 from electricity generating units (EGU). A cap was established on total EGU emissions of SO_2 in the conterminous United States. By 2009, the 3,572 EGUs covered by the ARP had reduced their combined SO_2 emissions by about two-thirds from 1980 levels. Ambient spatial patterns in SO_2 emissions are shown in Map 2 for the three-year average period centered on 2011, the latest three-year period for which a national emissions inventory is available at the time of this writing. Highest SO_2 emissions occurred in the eastern United States where emissions in many counties were higher than 50 tons of SO_2 per square mile per year (tons/mi^2/yr).

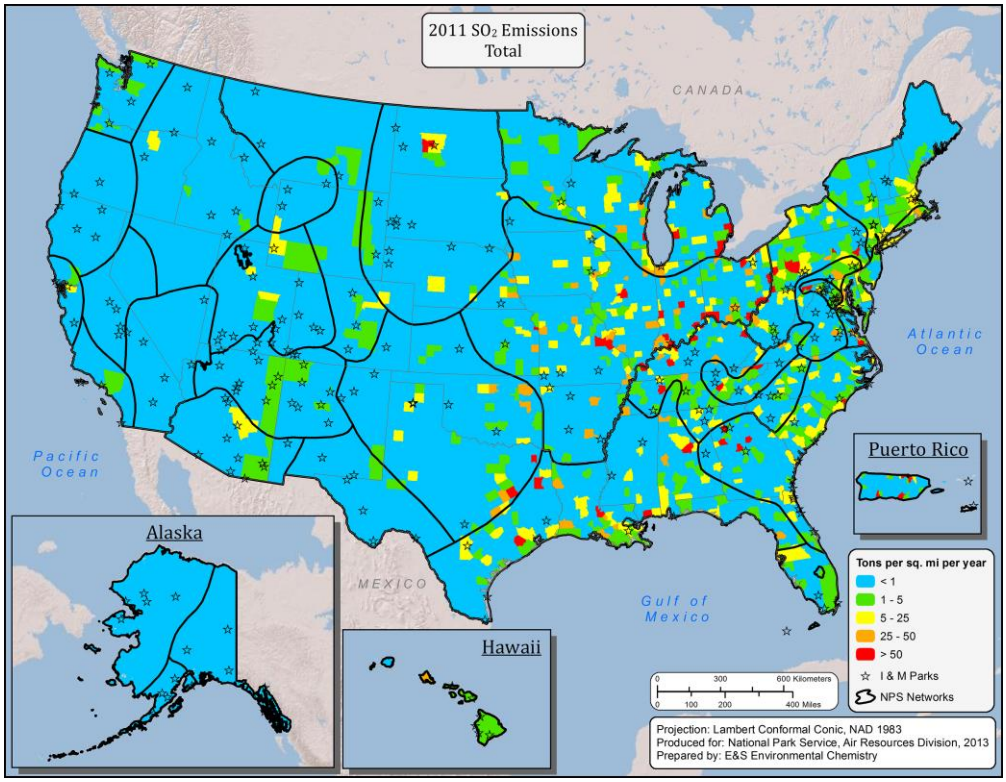
Emissions of NO_x in the United States derive mainly from power plants, motor vehicles, industry, and more recently O&G development. Reduced N (NH_3) emissions derive mainly from agricultural sources, including fertilizer and livestock waste. The 960 EGUs subject to ARP regulations governing NO_x emissions reduced their NO_x emissions by two-thirds between 1995 and 2009 (Burns et al. 2011). Nonpoint sources of NH_3 emissions remain largely uncontrolled, and deposition of these emissions has increased at most park locations over the last decade.

The NEI databases for 2002 and 2011 (http://www.epa.gov/ttnchie1/net/2011inventory.html) were used as the basis for mapping county total emissions of NO_x, NH_3, and SO_2 for this report. The NEI is prepared every three years by the EPA, based primarily upon emissions estimates and emissions model inputs provided by State, Local, and Tribal air agencies for sources in their jurisdictions, and supplemented by data developed by the EPA. Although there are uncertainties in the emissions estimates, they provide useful information on the amount and distribution of emissions quality and quantity and emissions sources. Emissions source types that comprised more than one percent of total national emissions were used as the basis for the mapped values presented here. The individual source types were grouped into broad categories, including agricultural, electricity generation, industrial and residential, fire, mobile, and biogenic. Table 3 describes the types of sources in each category.

a)



b)



Map 2. Total SO_2 emissions, by county, for the years a) 2002 and b) 2011, based on data from the NEI.

Table 3. Emissions source type groups used for mapping 2011 NEI emissions data.

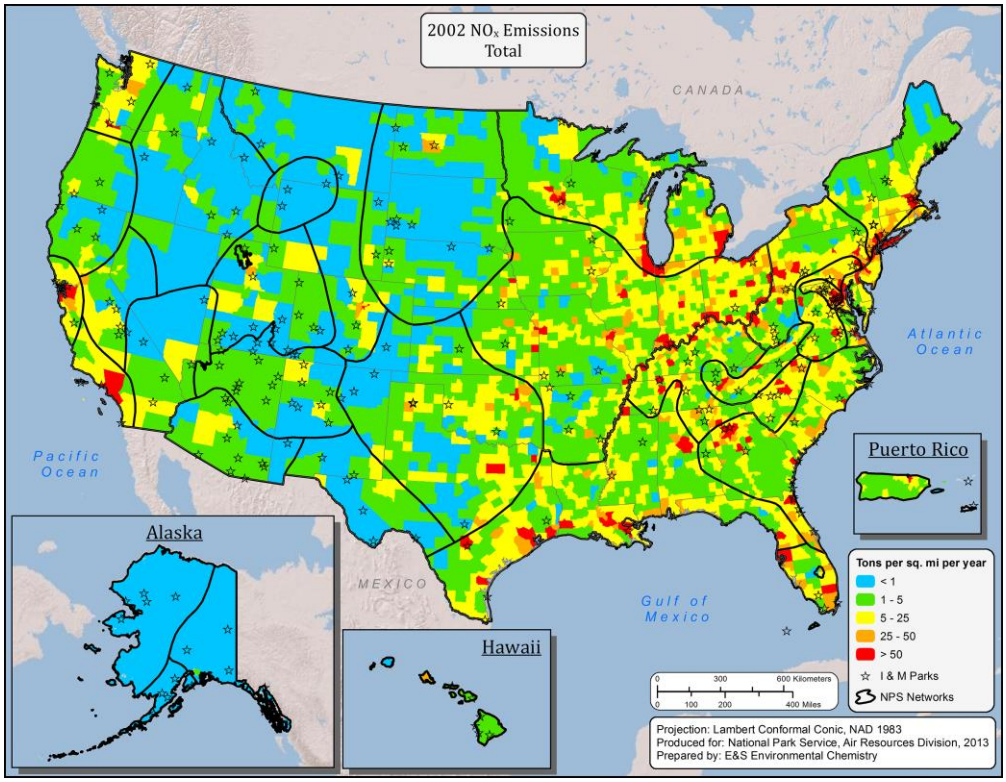
Emissions Source Group	Emissions Source Type from NEI[1]
Agriculture (Fertilizer Application)	Agriculture - Fertilizer Application
Agriculture (Livestock Waste)	Agriculture - Livestock Waste
Biogenics	Biogenics - Vegetation and Soil
Fire	Fires - Prescribed Fires
	Fires - Wildfires
Electricity Generation	Fuel Comb - Electric Generation - Coal
	Fuel Comb - Electric Generation - Natural Gas
	Fuel Comb - Electric Generation - Oil
Industrial and Residential	Fuel Comb - Industrial Boilers, ICEs - Coal
	Fuel Comb - Industrial Boilers, ICEs - Natural Gas
	Fuel Comb - Industrial Boilers, ICEs - Oil
	Fuel Comb - Residential - Natural Gas
	Fuel Comb - Residential - Oil
	Industrial Processes - Chemical Manufacturing
	Industrial Processes - NEC
	Industrial Processes - Non-ferrous Metals
	Industrial Processes - Oil & Gas Production
	Industrial Processes - Petroleum Refineries
	Waste Disposal
Mobile	Mobile - Commercial Marine Vessels
	Mobile - Locomotives
	Mobile - Non-Road Equipment - Diesel
	Mobile - Non-Road Equipment - Gasoline
	Mobile - On-Road Diesel Heavy Duty Vehicles
	Mobile - On-Road Gasoline Heavy Duty Vehicles
	Mobile - On-Road Gasoline Light Duty Vehicles

[1]ICE – internal combustion engine

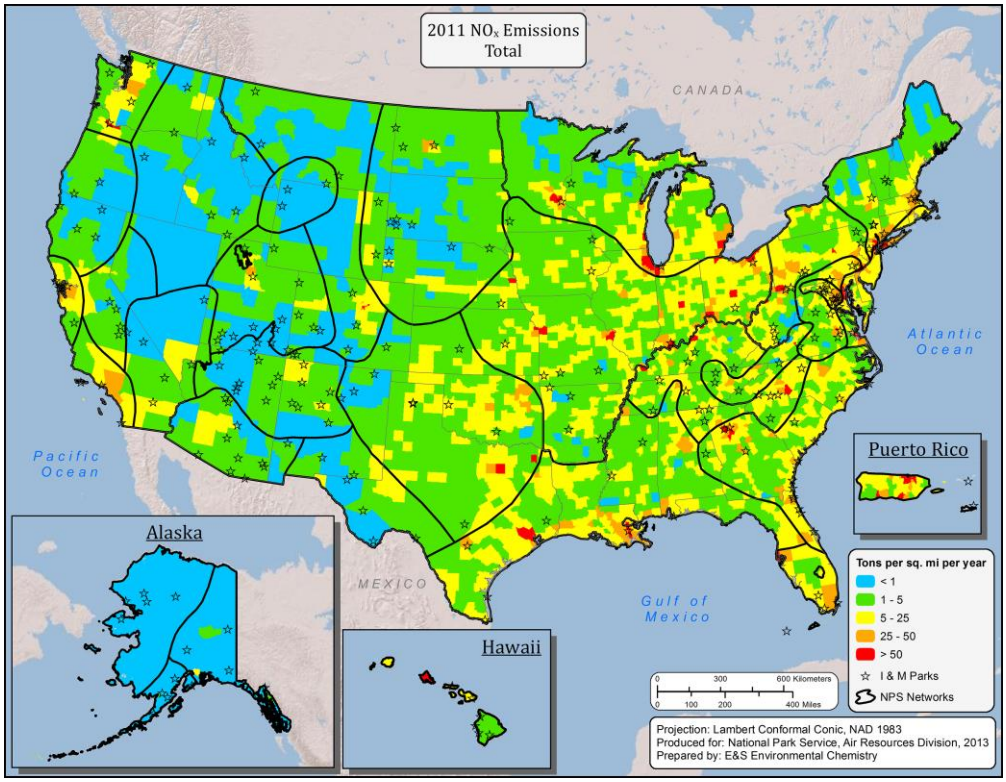
NEC – not elsewhere classified

Emissions from these aggregated source type categories were mapped for each county in units of tons/mi^2/yr for the years 2002 and 2011. Information for individual emissions sources can be found at http://www.epa.gov/ttn/chief/net/2011inventory.html. Spatial patterns in NO_x emissions are shown in Map 3 for the three-year periods centered on 2002 and 2011. Emissions of NO_x were above 5 tons/mi^2/yr in counties scattered throughout the conterminous United States, although counties in the East generally had larger emissions than those in the West.

a)



b)



Map 3. Total NO_x emissions, by county, for the years a) 2002 and b) 2011, based on data from the NEI.

Breakdowns of emissions, by source sector, are provided for SO_2, NO_x, and NH_3 sources in Appendix A. Information contained on those source sector maps is discussed briefly here. In addition, a series of maps is included in each of the network chapters of this report. These include network maps for emissions of SO_2, NOx, and reduced NH3. County-based emissions of SO_2 were generally highest at scattered locations throughout the eastern United States (Map 2). In contrast to the generally decreasing trends in SO_2 and NO_x emissions throughout the U.S. between 2002 and 2011 (Maps 2 and 3), NH_3 emissions have mostly stayed constant or increased (Map 4). The largest SO_2 sources were from electricity generation (Appendix A). Other SO_2 emissions sectors were generally relatively small contributors to total SO_2 emissions.

Spatial patterns in NO_x emissions showed that highest emissions were also generally in the eastern United States, with additional hot-spots of NO_x emissions near large urban areas along the west coast. The largest contributions to NO_x emissions were from the mobile source sector. The electricity generation and industrial and residential sectors were also important contributors (Appendix A).

Ammonia emissions were concentrated mainly in the Upper Midwest, with additional pockets of relatively high NH_3 emissions at locations along the east coast and in California. The largest NH_3 emissions sectors were agricultural (livestock and fertilizer application; Appendix A).

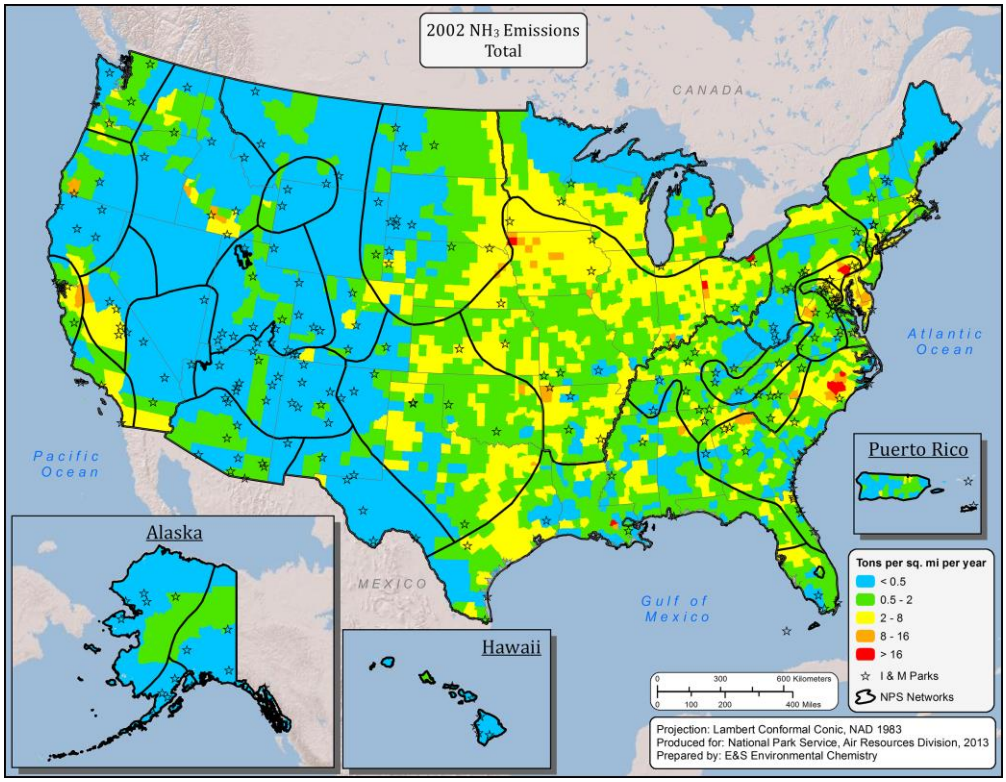
In addition to the ARP, a number of other programs have contributed to recent reductions in NO_x emissions in many areas, especially in the eastern United States. These have included a memorandum of understanding (1999-2002) among 11 states and the District of Columbia to implement NO_x control technologies and an O_3-season cap-and-trade program and also the NO_x State Implementation Plan (SIP) call issued in 1998 to reduce O_3 transport.

Total annual national emissions of SO_2 throughout the United States, as represented by the NEI, decreased from about 31 million tons in 1970 to about 5 million tons in 2012. Over that same time period, NO_x emissions decreased from about 28 million tons to 11 million tons. As emissions from regulated SO_x and NO_x sources decline, the relative importance of other sources is increasing. These include dust, international sources, and wildfire emissions (Hand et al. 2014).

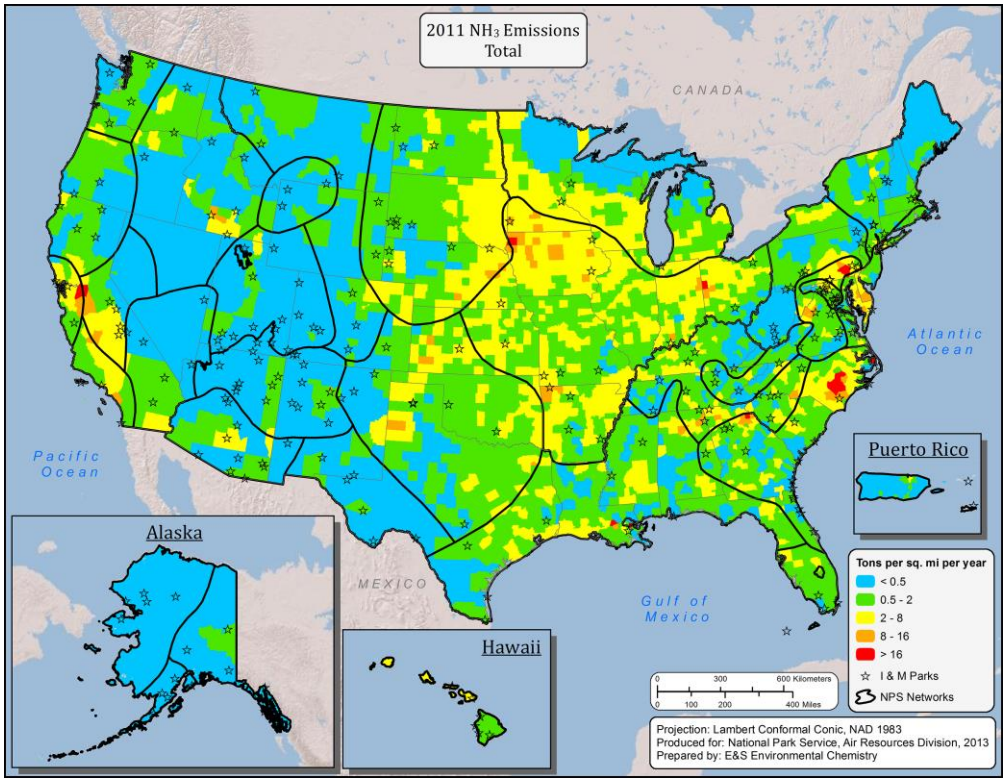
The Clean Air Interstate Rule (CAIR) was promulgated in 2005 to reduce emissions of SO_2 and NO_x. It was remanded by the courts in 2009, but has remained in place while EPA has worked on developing a replacement. Emissions reductions under this, and other, air pollution control programs have contributed to improvement in air quality as documented in measurements of ambient atmospheric concentrations of SO_x, NO_x, and O_3.

Emissions of NO_x and other pollutants from O&G development are rapidly emerging as an important threat to air quality in various regions of the United States. Recent and ongoing O&G development in the United States is accomplished mainly by hydraulic fracturing (fracking), which uses pressure from water and steam to fracture shale deposits to release oil and gas.

a)



b)



Map 4. Total NH_3 emissions, by county, for the years a) 2002 and b) 2011, based on data from the NEI.

Many thousands of new O&G wells have been installed in parts of the United States, most since about 2008, and the installation rate is expected to continue to increase (NPCA 2013). Emissions from an individual well are insignificant to the broader landscape. However, the cumulative effects of many thousands of wells may be substantial. Because the O&G source is increasing so rapidly, few data are available with which to assess the magnitude of the effects on N deposition, O_3 formation, and other air and water pollution issues. There is an accelerating need to compile and evaluate data on O&G emissions, deposition, and effects in and around many national parks.

Emissions of NO_x from traditional vertical drilling and from other vehicular and industrial sources also impact air quality and pollutant deposition in NPS parks. Emissions of ammonia from confined animal feeding operations (CAFOs) and other agricultural operations are important N sources in some regions.

Major sources of Hg emissions include coal-fired power plants, incinerators, and industry. The peak Hg deposition in much of the eastern United States occurred in the 1980s, with a substantial decrease since then (Drevnick et al. 2012). During the more recent decades, however, global anthropogenic Hg emissions increased 17% (Pirrone et al. 2010), to some degree negating the benefits of emissions reductions in the United States. Ambient Hg deposition is now about 3-4 times higher than pre-industrial deposition, based on analysis of lake sediment cores (Drevnick et al. 2012).

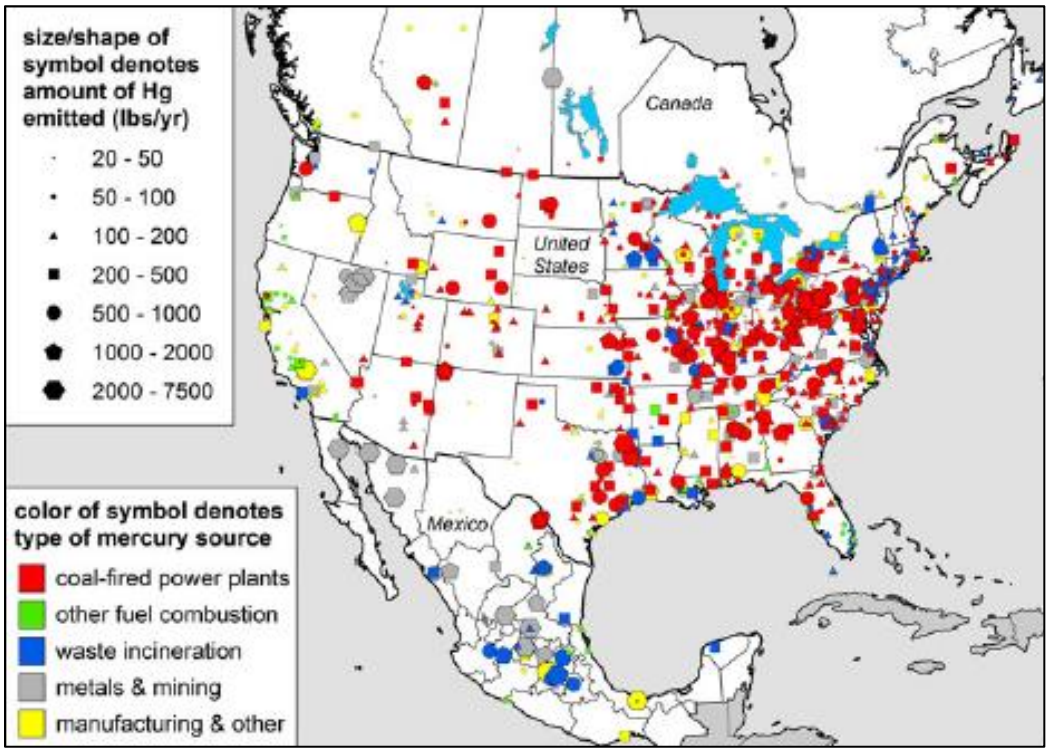
Because of its toxicity, standards for Hg emissions are expressed in pounds, rather than tons. Major sources of Hg emissions include coal-fired power plants, incinerators, and industry. The peak Hg deposition in much of the eastern United States occurred in the 1980s, with a substantial decrease since then (Drevnick et al. 2012) from 246 tons in 1990 to 101 tons in 2005 (U.S. EPA 2000, 2005). This decrease has largely been attributed to controls on municipal and medical waste incinerators (Butler et al. 2008). The largest single type of emissions source in 2005 was coal-fired power plants (52.3 tons emitted), followed by other boilers, cement manufacturing, and electric arc furnaces (Map 5; Schmeltz et al. 2011).

Although Hg emissions have decreased in the U.S., global anthropogenic Hg emissions increased 17% in recent decades (Pirrone et al. 2010), to some degree negating the benefits of emissions reductions in the United States. Ambient Hg deposition in the U.S. is now about 3-4 times higher than pre-industrial deposition, based on analysis of lake sediment cores (Drevnick et al. 2012).

During the past two decades, anthropogenic emissions of Hg in the United States have decreased dramatically, from 246 tons in 1990 to 101 tons in 2005 (U.S. EPA 2000, 2005). This decrease has largely been attributed to controls on municipal and medical waste incinerators (Butler et al. 2008). The largest single type of emissions source in 2005 was coal-fired power plants (52.3 tons emitted), followed by other boilers, cement manufacturing, and electric arc furnaces (Map 5; Schmeltz et al. 2011).

Toxic substances other than Hg are also emitted into the atmosphere from a variety of industrial, agricultural, and other sources. These include many pesticides. Emissions of current use pesticides (CUPs) derive mainly from agricultural sources. These include row crops and other forms of

intensive agriculture. There are also emissions, presumably mainly from the soil, of legacy pollutants, including pesticides, that are now banned or tightly controlled. Dioxins, polycyclic aromatic hydrocarbons (PAH), and other chemical byproducts are produced unintentionally and released to the atmosphere during combustion processes.



Map 5. Distribution of total Hg annual emissions from point sources in the United States, Canada, and Mexico. Total number of point sources in inventory is 15,892, which equals 155 tons/year (310,000 lbs/yr). Point sources not mapped are those under 20 lbs/year (n = 3,508). Point source emissions in Alaska and Hawaii are minor (under 20 lbs/year) and not depicted here. (Source: Schmeltz et al. 2011)

In some places, it is possible to identify probable individual sources of semivolatile organic compound (SOC) or other toxic contaminant emissions. For example, Snyder Lake watershed in GLAC exhibited higher PAH concentrations in snow, sediments, and vegetation than nearby Oldman Lake watershed, and 10 to 100 times higher PAH concentrations than watersheds in any other park included in the Western Airborne Contaminants Assessment Project (WACAP) study; this observation led to investigation of the Al smelter in Columbia Falls, Montana as an emissions source. After comparison of PAH levels in sediment from before and after initiation of smelter operations, it was identified as the likely primary source for the high levels of PAH deposition in that area (Landers et al. 2010, Usenko et al. 2010). WACAP results also suggested that the Continental Divide can be a geographical barrier to atmospheric transport of air contaminants. Measured SOC and Hg concentrations were higher in Rocky Mountain National Park (ROMO) sample sites on the east side of the divide as compared with the west side.

As the United States and Canada continue to reduce emissions of air pollutants to comply with existing standards and regulations, emissions of many pollutants are rapidly rising in developing countries, especially in Asia. These new global emissions may offset some of the gains that would otherwise accrue from local and regional emissions reductions in the U.S. (Jacob et al. 2011). Pollutants having short atmospheric lifetimes of a few days or less do not necessarily require global analysis. However, circumpolar atmospheric transport occurs over about four weeks, and transport from Asia to the conterminous United States typically takes only two to three weeks (Jacob et al. 2011). Thus, pollutants with atmospheric lifetimes longer than several weeks do warrant such a broad perspective.

Deposition

Airborne particles, their gas-phase precursors, and their transformation products are removed from the atmosphere by wet, dry, and occult (cloud and/or fog) deposition processes. These deposition processes transfer pollutants to other environmental media such as vegetation, soil, and exposed rock or water surfaces where they can alter the structure, function, diversity, and sustainability of complex ecosystems.

There are important differences among the various media and how pollutant amounts are expressed. Emissions are commonly expressed so as to reflect the quantity of pollutant emitted from a source into the atmosphere in units such as, for example, tons per year (tpy). Once in the atmosphere, the amount of pollutant may be expressed as an atmospheric concentration. This may be, for example, in units that reflect the amount of pollutant per cubic meter of air.

Wet deposition is calculated as the concentration of the pollutant in precipitation (rain and snow) times the amount of precipitation. It is expressed in units that reflect the amount of wet deposition pollutant transfer from the atmosphere to the ground/vegetation/water surfaces, per unit area, per unit time (often as kilograms per hectare per year [kg/ha/yr]).

Dry deposition transfers pollutants from the atmosphere to the ground/vegetation/water surfaces without precipitation as the transfer vehicle. It is estimated based on the pollutant atmospheric concentration and an assumed deposition velocity (or transfer rate). The actual amount of dry deposition is expressed as amount of pollutant that is dry deposited per unit ground or watershed area per unit time (often as kg/ha/yr).

There are differences in the deposition behavior of gaseous pollutants and fine and coarse particles. Coarse particles generally deposit nearer their site of formation than do fine particles or gasses. The chemical composition of individual particles is also related to particle size. For example, fine PM may act as a carrier for materials such as herbicides that are phytotoxic. Fine PM provides much of the surface area of particles suspended in the atmosphere, and in many areas are primarily responsible for visibility impairment, or haze, whereas coarse PM provides much of the mass of atmospheric particles. Surface area can influence ecological effects associated with the oxidizing capacity of fine particles, their interactions with other pollutants, and their adsorption of phytoactive organic compounds. Fine and coarse particles also respond to changes in atmospheric humidity, precipitation, and wind, and these can alter their deposition characteristics.

Atmospheric deposition can be the primary source of various metals to watersheds at remote locations. Metal inputs can include the primary crustal elements (aluminum [Al], calcium [Ca], potassium [K], iron [Fe], magnesium [Mg], silicon [Si], titanium [Ti]) and the primary anthropogenic elements (copper [Cu], zinc [Zn], cadmium [Cd], chromium [Cr], manganese [Mn], lead [Pb], vanadium [V]). The crustal elements are derived largely from weathering and erosion, whereas the anthropogenic elements are derived from combustion, industrial sources, and other human-caused sources (Goforth and Christoforou 2006). Many of the heavy metals (e.g., Cd, Cr, Pb) are toxic and can impair the functions of organisms and ecosystems.

Deposition of coarse and fine PM is generally highest in urban areas, derived from industrial processes, vehicular traffic, and home heating (Lu et al. 2003, Rocher et al. 2004). Urban settings, therefore, continue to be a major focus of atmospheric particulate research (U.S. EPA 2009b). Previous work tended to focus on the size of particles as a consequence of epidemiologic studies that found strong associations between particle size and human respiratory illness, with smaller particles able to penetrate deep into the respiratory system and cause harm. Studies have also assessed the chemical composition of particles and the processes involved in their formation (Gilli et al. 2007).

Some of the most useful records of long-term atmospheric PM deposition are recorded as accumulations of atmospherically deposited metals in ice, snow, peat, and lake sediments. Case studies presented by Norton (2007) focused on three elements (Cd, Pb, Hg), which are biologically active, have negative consequences for ecosystem and human health, and are dominated by atmospheric inputs. Sedimentary pollution records suggested that atmospheric deposition of these elements in the United States peaked in about the period 1965 to 1975, but subsequently declined by 75% or more. High concentrations still reside in soil in some areas, but the flux through aquatic ecosystems has decreased in recent decades (Norton 2007).

The earlier deposition estimates by Sullivan et al. (2011a, 2011b) for the time period centered on 2001 were generated from interpolated wet deposition measured by the National Atmospheric Deposition Program, National Trends Network (NADP/NTN) in 2002 and modeled dry deposition simulated by the Community Multiscale Air Quality (CMAQ) model (Byun and Schere 2006). At that time, the most recent CMAQ data available were for 2002. At the time of this writing, the most recent wet plus dry deposition data available are for the year 2012. Thus, deposition is expressed here as the average of data for 2010, 2011, and 2012. To evaluate changes in deposition over time, Total Deposition Science Committee (TDEP; Schwede and Lear 2014) estimates of deposition are compared for two time periods, as three-year averages centered on 2001 and 2011.

Wet Deposition

Pollutants are deposited into ecosystems through rain and snow as wet deposition. Wet deposition of S, N, Hg, base cations (Ca, Mg, sodium [Na], and K), and other elements is measured at individual monitoring stations by the National Atmospheric Deposition Program (NADP). They are located throughout the United States, including in about 40 national parks. Rain and snow are collected on a weekly basis and analyzed in a central laboratory for a variety of chemical species, which are reported as concentrations (e.g., milligrams per liter) or deposition (e.g., kg/ha/yr). Data are available from the NADP/National Trends Network (NTN), and the NADP/Mercury Deposition

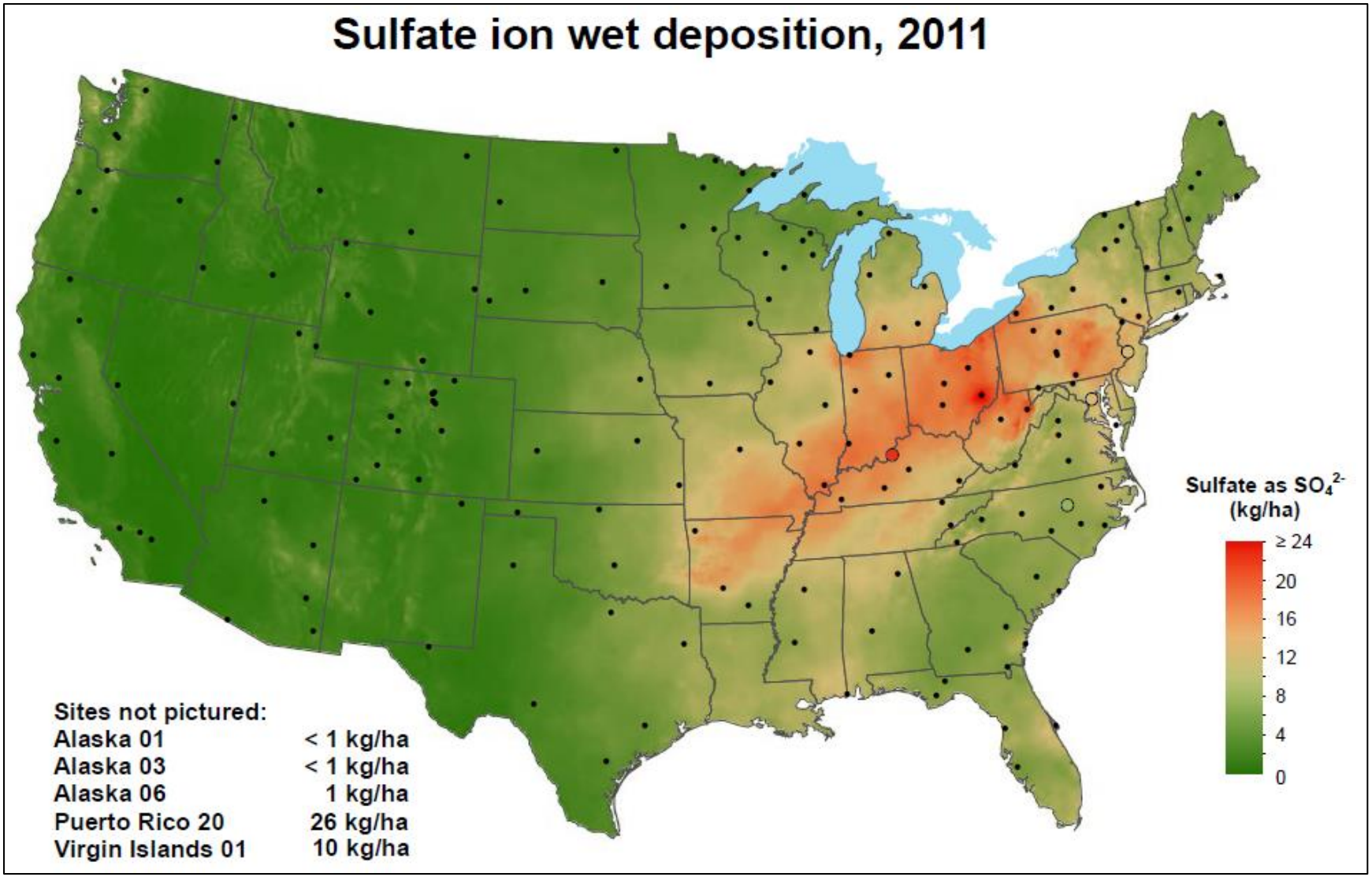
Network (MDN), with monitoring at some sites extending back to the early 1980s for S and N. Spatial patterns in wet deposition of sulfate (SO_4^{2-}), nitrate (NO_3^-), ammonium (NH_4^+), and Hg for a recent year (2011) are presented in Maps 6-9, respectively. Spatial patterns in SO_4^{2-} and NO_3^- wet deposition are generally similar, with highest values in a band from the Midwest to the Northeast. This reflects the prevalence of power plants, human population centers, and motor vehicles in these areas. Ammonium wet deposition shows highest values throughout the Midwest and other areas of intensive agricultural development. Available data are generally assumed to well represent geographic patterns in wet deposition, although high elevation areas (which often receive proportionately higher levels of wet deposition) are less well represented. Wet Hg deposition tends to be highest in summer (MDN: http://nadp.sws.uiuc.edu/MDN/why.aspx). It is especially high in Indiana, Ohio, Illinois, and portions of Pennsylvania, Michigan, and Wisconsin (Map 9; Risch et al. 2012, Wiener et al. 2012).

Most of the Hg emitted to the atmosphere deposits as reactive Hg (Hg(II)) . The reactive species of Hg are more readily removed from the atmospheric than is elemental Hg. Particulate Hg is readily wet deposited due to cloud scavenging processes and precipitation. Elemental Hg can be converted in the atmosphere to a gaseous form, which is more soluble and chemically reactive. This makes it more easily deposited to land surfaces via wet deposition.

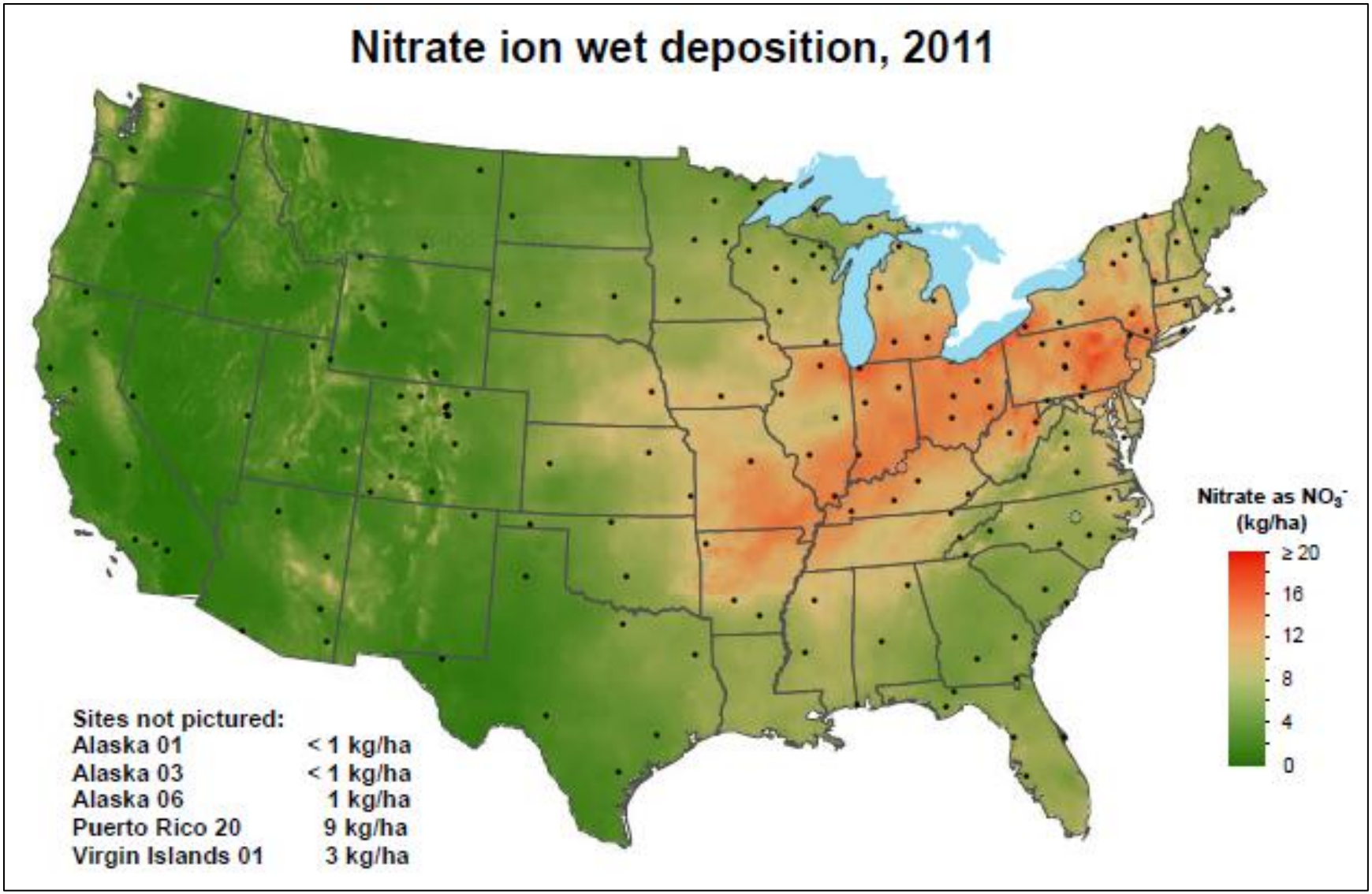
Dry Deposition

In general, wet deposition measurements collected in the various monitoring networks are considered to be relatively robust. Scientists generally place rather high confidence in these measurements. In contrast, measurements of dry deposition, described below, take multiple forms and are much more uncertain. This can be problematic because most ecological effects reflect total (wet plus dry, and [where important] also occult]) deposition. Furthermore, dry inputs can constitute half or more of the total at many locations.

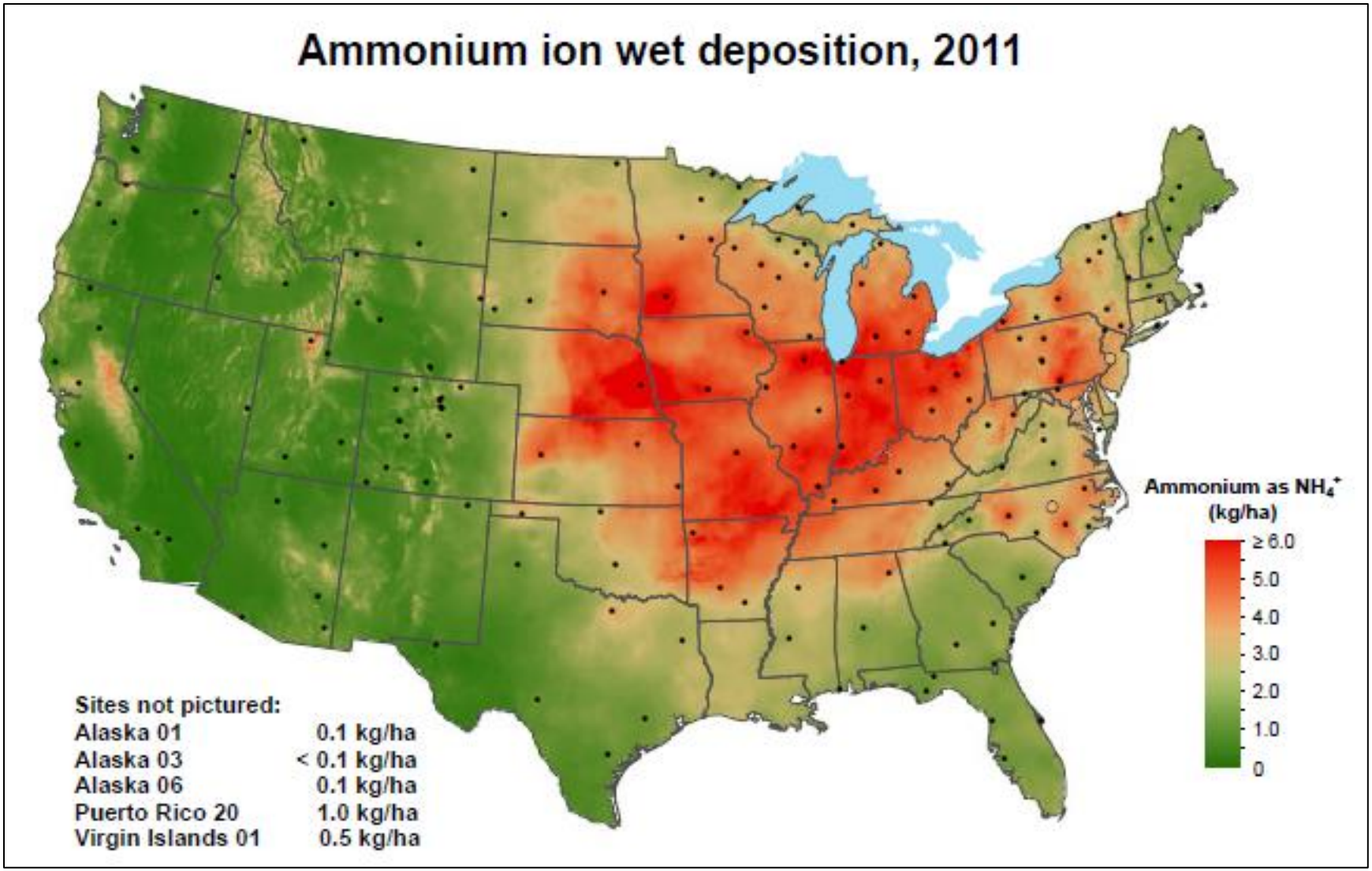
Mercury gases and particles, including elemental Hg, can be directly deposited to land upon contact as dry deposition. This is especially important in forested areas, where Hg is deposited to tree foliage and then transported to the soil through leaf fall. A portion of wet deposited Hg to forest canopies may be photo-reduced and then re-emitted to the atmosphere. Gustin et al. (2006) showed that re-emission of deposited Hg from soil can be affected by environmental conditions such as soil moisture, temperature, light, the presence of atmospheric oxidants, and Hg concentrations in air (U.S. EPA 2009b).



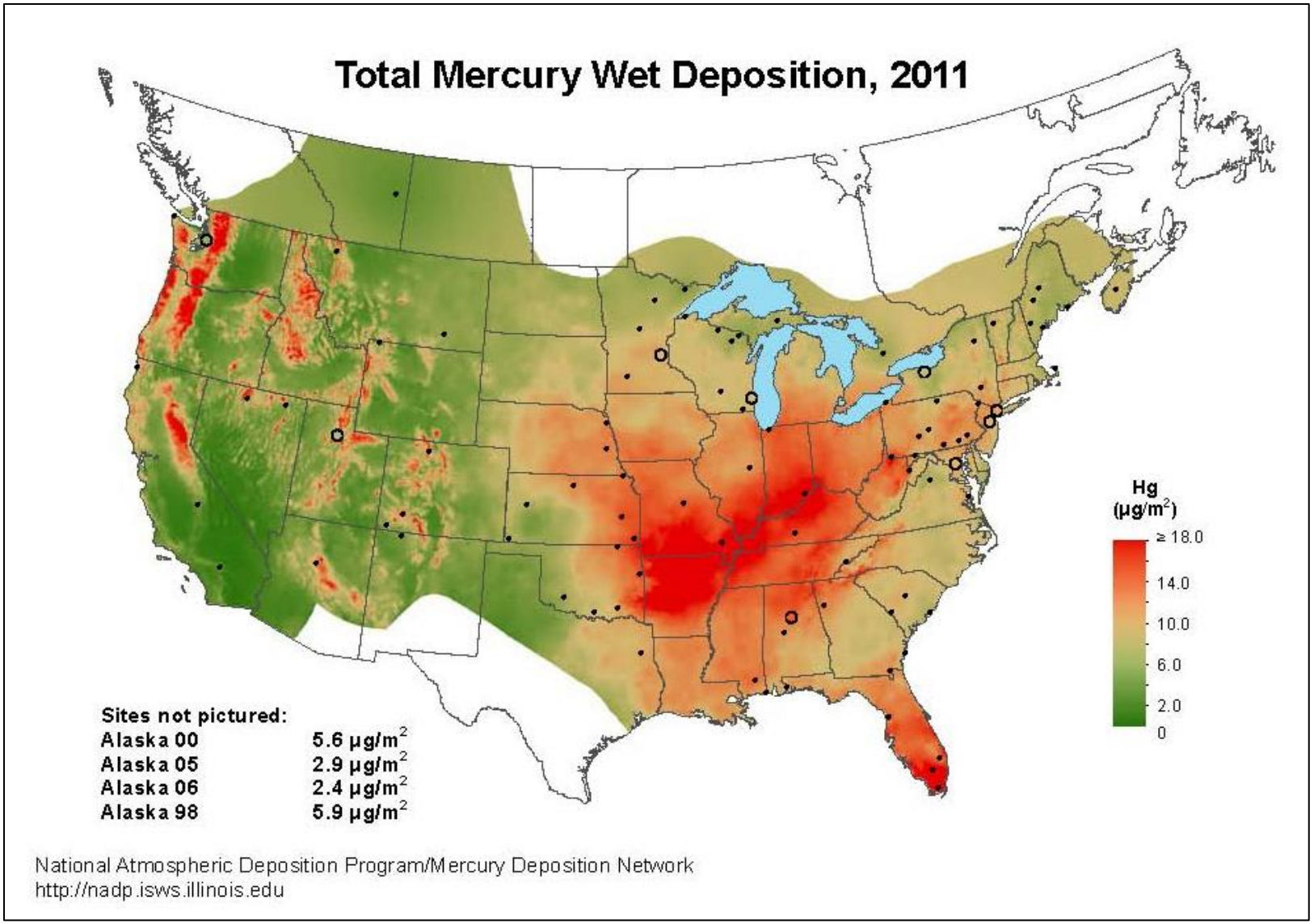
Map 6. Wet SO_4^{2-} deposition throughout the United States for the most recent year available at the time of this writing. (Source: NADP/NTN) Black dots mark site locations that meet NADP completeness criteria. Open circles designate urban sites, defined as having at least 400 people per square kilometer within a 15-km radius of the site. Urban sites do not contribute to the contour surface.



Map 7. Wet NO_3^- deposition throughout the United States for the most recent year available at the time of this writing. (Source: NADP/NTN) Black dots mark site locations that meet NADP completeness criteria. Open circles designate urban sites, defined as having at least 400 people per square kilometer within a 15-km radius of the site. Urban sites do not contribute to the contour surface.



Map 8. Wet NH_4^+ deposition throughout the United States for the most recent year available at the time of this writing. (Source: NADP/NTN) Black dots mark site locations that meet NADP completeness criteria. Open circles designate urban sites, defined as having at least 400 people per square kilometer within a 15-km radius of the site. Urban sites do not contribute to the contour surface.



Map 9. Interpolated wet Hg deposition for 2011 determined by the Mercury Deposition Network. (Source: NADP MDN) Black dots mark site locations that meet NADP completeness criteria. Open circles designate urban sites, defined as having at least 400 people per square kilometer within a 15-km radius of the site. Urban sites do not contribute to the contour surface.

Pollutants are deposited as dry deposition into ecosystems through particles, aerosols, and gases. Dry deposition generally cannot be directly measured. Dry deposition rates and totals are often calculated as the product of measured ambient atmospheric concentration and a modeled deposition velocity. This method is widely used because atmospheric concentrations are easier to measure than are dry deposition rates, and models have been developed to estimate deposition velocities. The National Dry Deposition Network (NDDN) was established in 1986 to document the magnitude, spatial variability, and trends in dry deposition across the United States. The network operates as a component of the Clean Air Status and Trends Network (CASTNET; Clarke et al. 1997). Ambient pollutant concentrations and meteorological conditions required for application of inferential models are routinely collected on a weekly basis at CASTNET dry deposition sites. Monitored chemical species include O_3, SO_4^{2-}, NO_3^-, NH_4^+, SO_2, and nitric acid (HNO_3), which are reported as concentrations in the atmosphere (e.g., micrograms per cubic meter) or deposition loading (e.g., kg/ha/yr).

Dry particulate deposition, especially of heavy metals, base cations, and organic contaminants, is a complex, poorly characterized process. It appears to be controlled primarily by such variables as atmospheric stability, macro- and micro-surface roughness, particle diameter, and surface characteristics (Hosker and Lindberg 1982). The range of particle sizes, diversity of vegetation canopy surfaces, and variety of chemical constituents in airborne PM have made it difficult to predict and to estimate dry particulate deposition (U.S. EPA 2004).

Estimates of regional particulate dry deposition infer fluxes from the product of variable and uncertain particulate concentrations in the atmosphere and even more variable and uncertain measured or modeled estimates of the deposition velocity parameterized for a variety of specific surfaces (e.g., Brook et al. 1999). Even for specific sites and well defined particles, uncertainties are large (U.S. EPA 2009b).

Collection and analysis of stem flow and throughfall can provide useful estimates of dry deposition when compared to directly sampled precipitation. This method is most precise when gaseous deposition is a small component of the total dry deposition and when the leaching or uptake of compounds of interest out of or into the foliage is not a significant fraction of the total depositional flux. This approach works relatively well for S, but not for N because N is an important nutrient that is often strongly taken up by plant foliage.

The plant leaf surface has an important influence on the deposition velocity of particles, and therefore on the rate of dry deposition to the terrestrial environment. Conifer needles are more efficient than broad leaves in collecting particles by impaction, reflecting the small cross section of the needles relative to the larger leaf laminae of broadleaves and the greater penetration of wind into conifer, as compared with broadleaf, canopies (U.S. EPA 2004). Canopies of uneven age or with a diversity of species are typically aerodynamically rougher and receive larger inputs of dry-deposited pollutants than do smooth, low, or monoculture vegetation (Garner et al. 1989, U.S. EPA 2004). Canopies on slopes facing the prevailing winds receive larger inputs of pollutants than more sheltered, interior canopy regions.

Estimates of total wet plus dry deposition of S and N throughout the conterminous United States are shown on Maps 10 and 11, respectively. Total S deposition is highest in the northeastern United States and along the Appalachian Mountains. Relatively high total N deposition occurs more sporadically throughout the eastern half of the country and in southern California. Current total N deposition in the intermountain West may be somewhat higher than is represented on Map 11 due to recent increased O&G development that has occurred subsequent to 2012 in some regions and the fact that much of the O&G emissions are not included in the NEI that formed the basis for TDEP deposition modeling. The total amount of deposited N is comprised of both oxidized N (Map 12) and reduced N (Map 13). Relatively high deposition of oxidized N is broadly associated with centers of human population in the eastern half of the country and in southern California. Relatively high deposition of reduced N is more closely associated with centers of agricultural development.

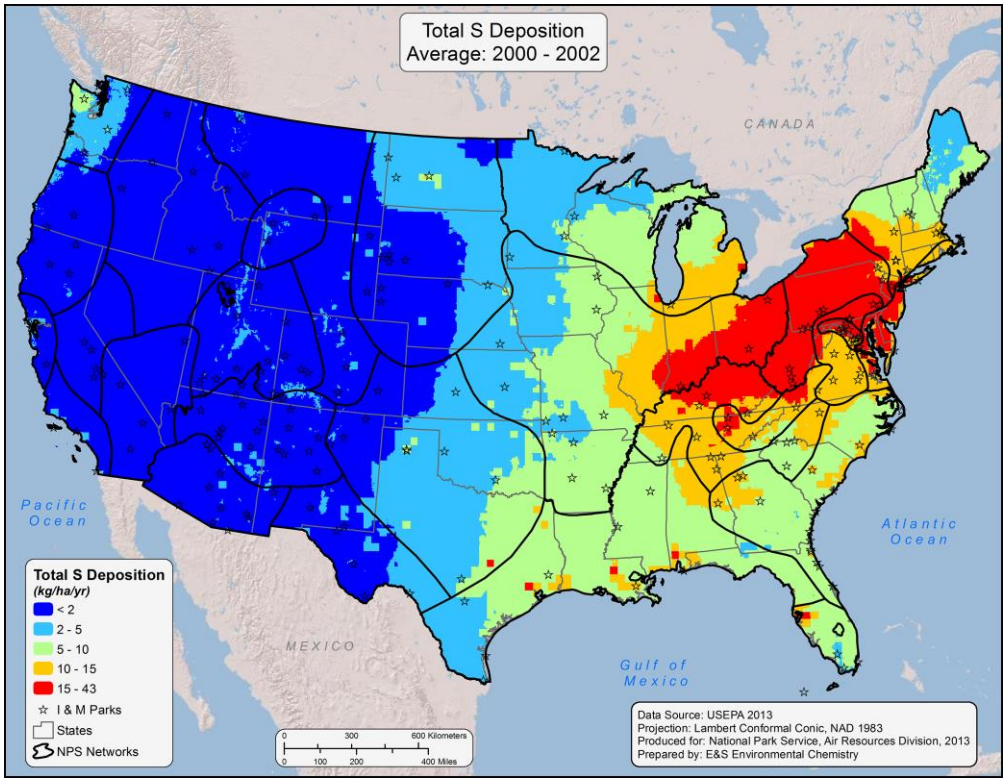
Occult Deposition

The occurrence of occult (cloud and/or fog) deposition tends to be more restricted geographically, mainly to coastal and high mountain areas. In some areas, typically along foggy coastlines or at high elevations, occult deposition represents a substantial fraction of total deposition of S and N to foliar surfaces (Fowler et al. 1991).

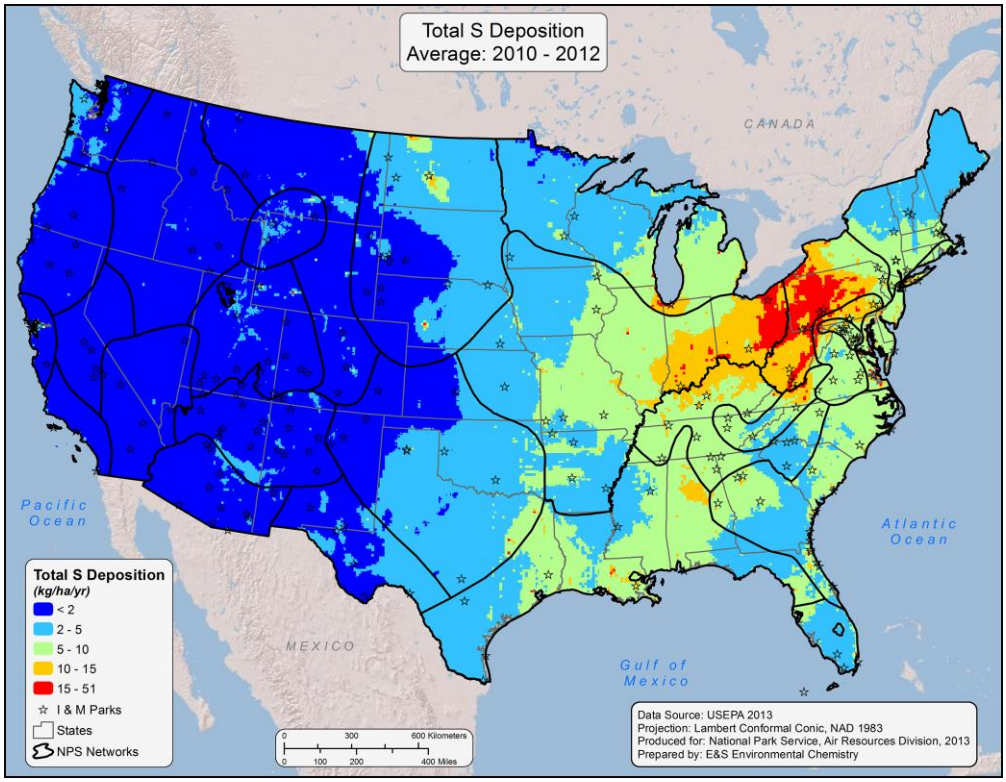
Several factors make occult deposition particularly effective, where it occurs, for the delivery of dissolved and suspended particulates to vegetation (U.S. EPA 2009b). Concentrations of particulate-derived materials are often many-fold higher in cloud or fog water than in precipitation or ambient air due to orographic effects and gas-liquid partitioning. In addition, fog and cloud water deliver chemical particle constituents in a bioavailable hydrated form to foliar surfaces.

Cloud water is often 5 to 20 times more acidic than rain water (Mohnen 1990, Vong et al. 1991), and clouds can contribute as much, or more, acidic deposition as do wet plus dry deposition processes at high-elevation sites (Fuzzi and Wagenbach 1997, Lovett and Kinsman 1990, Vong et al. 1991). Anderson et al. (1999) presented results of cloud chemistry measurements at three high-elevation sites in the eastern United States: Whiteface Mountain, NY; Whitetop Mountain, VA; and Clingman's Dome, TN. The most prevalent ions in cloud water, in decreasing order of importance, were SO_4^{2-}, H^+, NH_4^+, and NO_3^-. Variations in ionic concentrations were largely due to differences in liquid water content of cloud deposition samples. Cloud water sampling was discontinued at most sites but continued as the Mountain Acid Deposition Program (MADPro) at Clingman's Dome in Great Smoky Mountains National Park (GRSM) through 2011, when the program was finally terminated (AMEC Environment & Infrastructure Inc. 2013). The Adirondack Lakes Survey Corporation continues to monitor cloud deposition at Whiteface Mountain in New York (Dukett et al. 2011).

a)

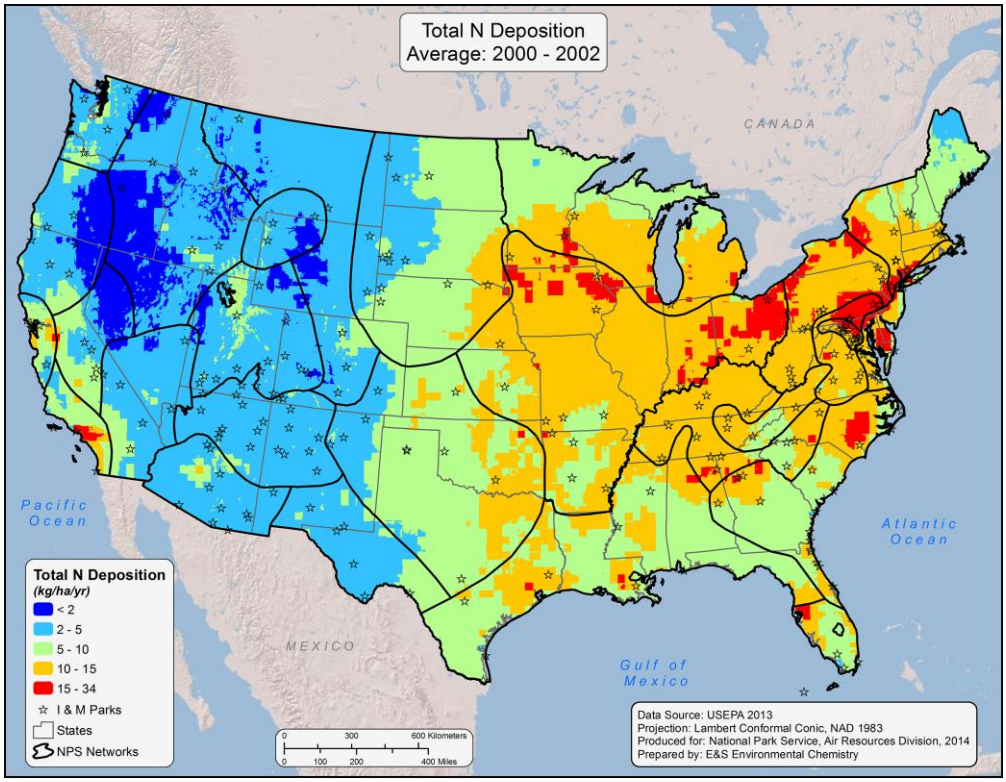


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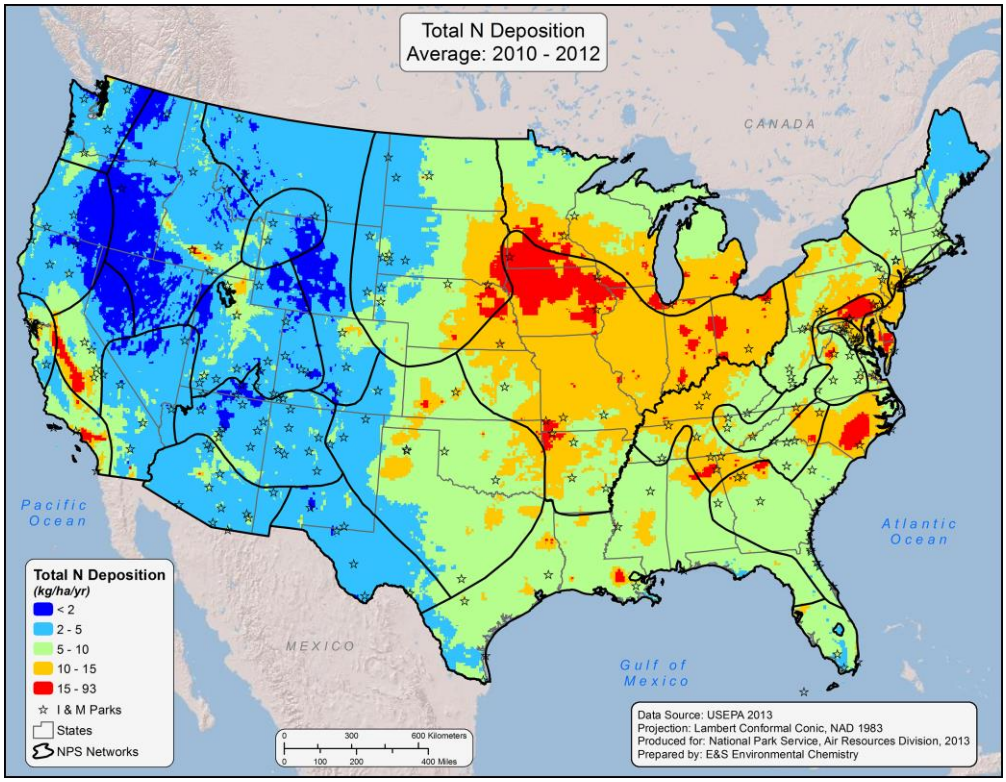


Map 10. Total annual S deposition throughout the conterminous United States based on TDEP estimates for a three-year average centered on a) 2001 and b) 2011.

a)

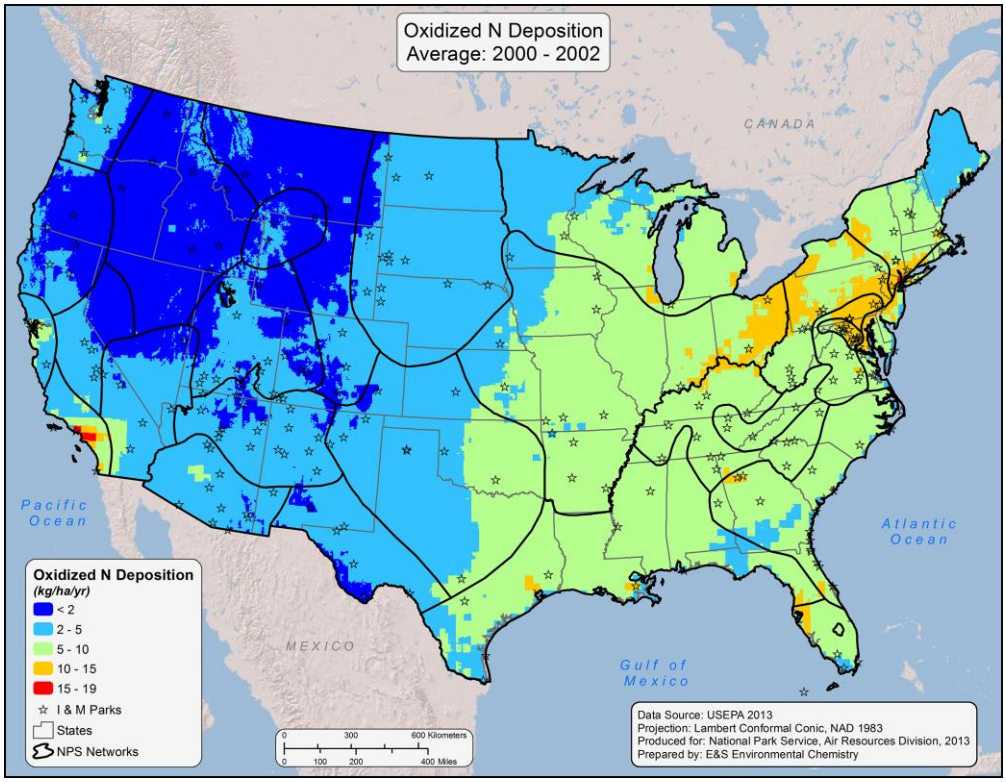


b)

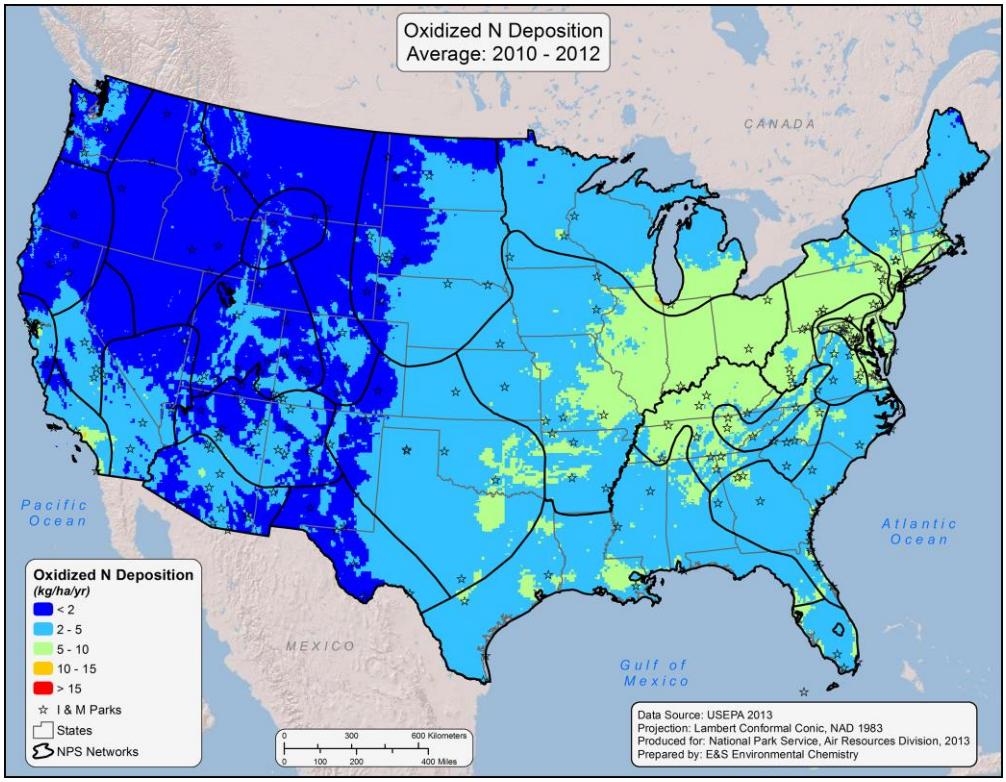


Map 11. Total annual N deposition throughout the conterminous United States based on TDEP estimates for a three-year average centered on a) 2001 and b) 2011.

a)

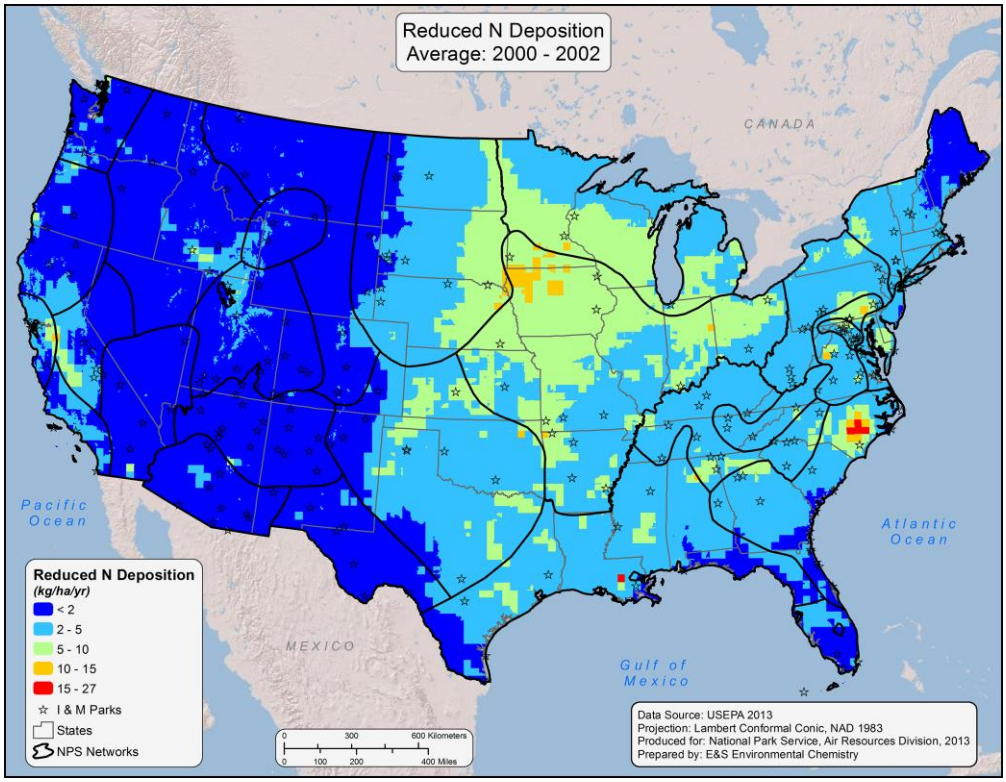


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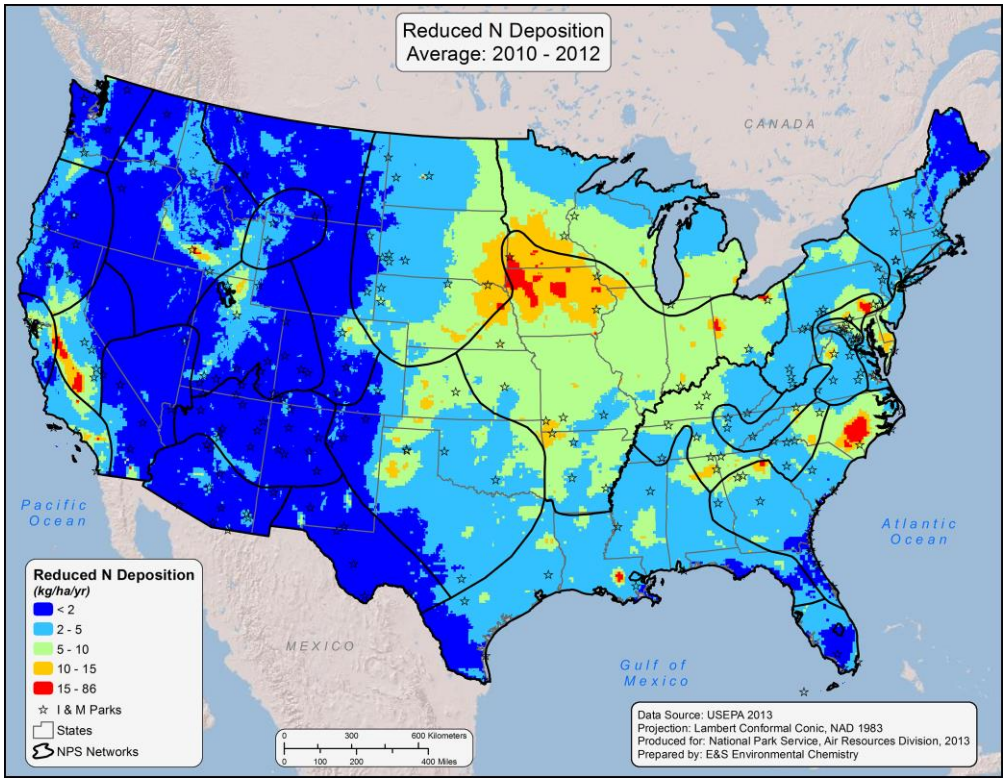


Map 12. Total annual oxidized inorganic N deposition throughout the conterminous United States based on TDEP estimates for a three-year average centered on a) 2001 and b) 2011.

a)



b)



Map 13. Total annual reduced inorganic N deposition throughout the conterminous United States based on TDEP estimates for a three-year average centered on a) 2001 and b) 2011.

Deposition estimates were obtained for this assessment from the recent effort by federal agencies in conjunction with the TDEP Science Committee of the NADP, to develop improved estimates of total atmospheric deposition (Schwede and Lear 2014). The TDEP estimates were calculated using a hybrid approach that combines measured and modeled estimates of wet and dry deposition to calculate total deposition. Monitoring data from CASTNET, the Ammonia Monitoring Network (AMoN), the Southeastern Aerosol Research and Characterization (SEARCH) network (rural sites only), and the NTN were used for generating TDEP estimates. Table 4 provides information on the measurement data used from each monitoring network. The CMAQ model was used as the basis for modeled estimates of deposition. The total deposition estimates provided by TDEP were produced at 4-km resolution using a method that combines monitoring data with output from the CMAQ modeling system. This method gives priority to measurement data near the location of the monitors and priority to CMAQ simulations in areas where monitoring data are not available.

CMAQ output is used for species such as peroxyacetyl nitrate (PAN), oxides of N (N_2O_5, NO, NO_2, HONO), and organic NO_3^- that are not routinely measured in the monitoring networks, but likely contribute a significant amount to the total N budget at some locations. However, TDEP estimates of wet and dry organic N deposition are likely underestimated and future TDEP releases are expected to have a more complete representation of organic N deposition. TDEP estimates of total deposition are just that, estimates. It cannot necessarily be assumed that they are correct. However, they are available at a relatively fine scale (4 km) throughout the conterminous United States. In addition, it is hoped that they may be more correct than other available estimates (McDonnell and Sullivan 2014). There are insufficient monitoring data available for Alaska, the Pacific Islands, and the Caribbean to generate modeled deposition estimates for those areas. Also, organic N is not routinely measured by the national deposition monitoring networks, but may contribute significantly to total N deposition in some areas (Cornell 2011). Efforts by the various monitoring networks and the modeling community continue to improve deposition estimates.

Table 4. Summary of data from monitoring networks used to derive TDEP estimates.

Network	Chemical Species[1]	Period of Record	Website
Clean Air Status and Trends Network (CASTNET)	Concentration: HNO3, SO2, pSO4, pNO3, pNH4	2000-2012	http://epa.gov/castnet/javaweb/index.html
Ammonia Monitoring Network (AMoN)	Concentration: NH3	2008-2012	http://nadp.sws.uiuc.edu/AMoN/
Southeastern Aerosol Research and Characterization (SEARCH)	Concentration: HNO3, SO2, NH3	2005-2011	http://www.atmosphericresearch.com/studies/SEARCH/
National Trends Network	Wet deposition: SO4, NO3, NH4	2000-2012	http://nadp.sws.uiuc.edu/NTN/

[1] the symbol p denotes particulate species

Between 2001 and 2011, S deposition at I&M parks decreased by varying amounts in many park networks (Table 5; Map 10). The median decrease was more than 5 kg S/ha/yr in the National Capital (NCRN), Appalachian Highlands (APHN), Eastern Rivers and Mountains (ERMN) Mid-Atlantic (MIDN), and Northeast Temperate (NETN) networks, all located in the eastern United States. The median park in all networks either decreased in S deposition during that ten-year time period or only increased by a small amount (+ 0.7 kg S/ha/yr in the Mediterranean Coast Network [MEDN] or less). Oxidized N deposition at the median park decreased in all networks (Table 6), with some decreases larger than 3 kg N/ha/yr (MEDN, NCRN, NETN, Cumberland Piedmont Network (CUPN], ERMN, MIDN). Conversely, all networks except ERMN and the Great Lakes Network (GLKN) showed increases in reduced N deposition (and those two networks showed only very small decreases (-0.1 kg N/ha/yr; Table 7). Total oxidized plus reduced N exhibited variable responses, with some networks showing decreases and some showing increases (Table 8). The largest decreases were in ERMN (-3.5 kg N/ha/yr), NETN(-3.2 kg N/ha/yr, MIDN (-2.9 kg N/ha/yr), and NCRN (-2.6 kg N/ha/yr). The largest median increases were smaller and occurred in the Sierra Nevada (SIEN; +1.4 kg N/ha/yr) and Heartland (+0.6 kg N/ha/yr) networks.

Particulate Matter

Fine PM is often a secondary pollutant that forms within the atmosphere, rather than being directly emitted from a pollution source. Secondary PM derives from atmospheric gas-to-particle conversion reactions involving nucleation, condensation, and coagulation, and from evaporation of water from contaminated fog and cloud droplets. Fine PM may also contain condensates of VOCs, volatilized metals, and products of incomplete combustion, including PAH and soot (U.S. EPA 2004).

Coarse PM is mainly a primary pollutant, having been emitted from pollution sources as fully formed particles derived from abrasion and crushing processes, soil disturbance, desiccation of marine aerosols emitted from bursting bubbles, hygroscopic fine PM expanding with humidity to coarse mode, and/or gas condensation directly onto preexisting coarse particles (U.S. EPA 2009b).

Suspended primary coarse PM may contain Fe, Si, Al, and base cations from soil, plant and insect fragments, pollen, fungal spores, bacteria, and viruses, as well as fly ash, brake lining particulates, debris, and automobile tire fragments.

In many rural areas and some urban areas, the majority of the mass in the atmospheric coarse particle mode derives from the elements Si, Al, Ca, and Fe, suggesting a crustal origin as fugitive dust from disturbed land, roadways, agriculture tillage, or construction activities. Rapid sedimentation of coarse particles tends to restrict their direct effects on vegetation largely to roadsides and forest edges, which often receive the greatest coarse particle deposition (U.S. EPA 2004).

Table 5. Distribution of estimated change from 2001 to 2011 in total sulfur deposition across I&M parks in each of the NPS Inventory and Monitoring networks in the conterminous United States, derived by the Total Deposition project (Schwede and Lear 2014). Deposition estimates are based on three-year averages centered on the years 2001 and 2011.

Network Code	Network Name	Number of Parks	Changes in Deposition (kg S/ha/yr)		
			Minimum	Median	Maximum
APHN	Appalachian Highlands	4	-8.2	-6.7	-4.2
CHDN	Chihuahuan Desert	6	-0.1	0.3	0.9
CUPN	Cumberland Piedmont	14	-9.3	-4.8	-2.8
ERMN	Eastern Rivers and Mountains	9	-16.4	-6.5	1.7
GLKN	Great Lakes	9	-2.9	-0.3	5.7
GRYN	Greater Yellowstone	3	0.2	0.3	0.3
GULN	Gulf Coast	8	-2.6	-0.6	0.8
HTLN	Heartland	15	-9.1	-0.7	0.3
KLMN	Klamath	6	0.0	0.2	0.6
MEDN	Mediterranean Coast	3	-0.4	0.7	2.1
MIDN	Mid Atlantic	10	-10.1	-6.3	-2.9
MOJN	Mojave Desert	6	0.0	0.0	0.2
NCBN	Northeast Coastal and Barrier	8	-9.5	-4.8	2.0
NCCN	North Coast and Cascades	7	-3.5	-0.6	0.1
NCPN	Northern Colorado Plateau	16	-0.3	-0.1	3.5
NCRN	National Capital Region	11	-9.1	-7.0	-5.6
NETN	Northeast Temperate	11	-7.3	-5.6	-3.3
NGPN	Northern Great Plains	13	-0.9	0.1	0.5
ROMN	Rocky Mountain	6	-0.3	-0.1	0.4
SCPN	Southern Colorado Plateau	19	-0.5	-0.1	0.5
SECN	Southeast Coast	17	-4.7	-2.8	0.6
SFAN	San Francisco Bay Area	6	-0.8	-0.1	3.0
SFCN	South Florida/Caribbean	4	-1.2	-0.9	-0.1
SIEN	Sierra Nevada	4	0.2	0.2	0.2
SODN	Sonoran Desert	11	-0.2	0.0	0.1
SOPN	Southern Plains	10	-3.4	-0.8	0.0
UCBN	Upper Columbia Basin	8	0.0	0.1	0.3

Table 6. Distribution of estimated change from 2001 to 2011 in total oxidized inorganic nitrogen deposition across I&M parks in each of the park networks in the conterminous United States, derived by the Total Deposition project (Schwede and Lear 2014). Deposition estimates are based on three-year averages centered on the years 2001 and 2011.

Network Code	Network Name	Number of Parks	Changes in Deposition (kg N/ha/yr)		
			Minimum	Median	Maximum
APHN	Appalachian Highlands	4	-3.2	-2.6	-1.8
CHDN	Chihuahuan Desert	6	-0.7	-0.4	-0.1
CUPN	Cumberland Piedmont	14	-4.1	-3.0	-1.9
ERMN	Eastern Rivers and Mountains	9	-4.6	-3.4	-2.4
GLKN	Great Lakes	9	-3.0	-1.6	0.2
GRYN	Greater Yellowstone	3	-0.3	-0.3	-0.3
GULN	Gulf Coast	8	-5.4	-1.9	0.0
HTLN	Heartland	15	-4.3	-0.9	-0.3
KLMN	Klamath	6	-1.0	-0.4	-0.4
MEDN	Mediterranean Coast	3	-7.0	-4.3	0.1
MIDN	Mid Atlantic	10	-4.6	-3.9	-2.3
MOJN	Mojave Desert	6	-1.4	-0.6	0.0
NCBN	Northeast Coastal and Barrier	8	-7.0	-2.5	2.8
NCCN	North Coast and Cascades	7	-1.2	-0.4	0.4
NCPN	Northern Colorado Plateau	16	-1.1	-0.5	0.1
NCRN	National Capital Region	11	-5.1	-3.7	-2.9
NETN	Northeast Temperate	11	-5.9	-3.5	-1.2
NGPN	Northern Great Plains	13	-0.8	-0.5	0.2
ROMN	Rocky Mountain	6	-0.6	-0.3	-0.1
SCPN	Southern Colorado Plateau	19	-1.4	-0.3	0.7
SECN	Southeast Coast	17	-6.4	-2.9	0.5
SFAN	San Francisco Bay Area	6	-8.1	-2.4	-0.6
SFCN	South Florida/Caribbean	4	-2.5	-2.1	-1.0
SIEN	Sierra Nevada	4	-0.3	-0.1	0.1
SODN	Sonoran Desert	11	-0.8	-0.4	0.1
SOPN	Southern Plains	10	-1.3	-1.0	0.1
UCBN	Upper Columbia Basin	8	-0.4	-0.3	0.0

Table 7. Distribution of estimated change from 2001 to 2011 in total reduced inorganic nitrogen deposition across I&M parks in each of the park networks in the conterminous United States, derived by the Total Deposition project (Schwede and Lear 2014). Deposition estimates are based on three-year averages centered on the years 2001 and 2011.

Network Code	Network Name	Number of Parks	Changes in Deposition (kg N/ha/yr)		
			Minimum	Median	Maximum
APHN	Appalachian Highlands	4	0.7	0.9	1.0
CHDN	Chihuahuan Desert	6	-0.1	0.0	0.1
CUPN	Cumberland Piedmont	14	0.0	1.2	3.5
ERMN	Eastern Rivers and Mountains	9	-0.3	-0.1	0.1
GLKN	Great Lakes	9	-0.6	-0.1	1.2
GRYN	Greater Yellowstone	3	0.1	0.7	1.0
GULN	Gulf Coast	8	-0.5	0.2	0.9
HTLN	Heartland	15	-0.2	1.8	5.5
KLMN	Klamath	6	0.2	0.6	0.8
MEDN	Mediterranean Coast	3	0.1	2.6	3.1
MIDN	Mid Atlantic	10	-1.3	0.8	2.3
MOJN	Mojave Desert	6	0.3	0.5	0.9
NCBN	Northeast Coastal and Barrier	8	-1.0	0.2	2.7
NCCN	North Coast and Cascades	7	0.2	0.3	1.0
NCPN	Northern Colorado Plateau	16	0.0	0.3	2.3
NCRN	National Capital Region	11	0.4	1.2	3.5
NETN	Northeast Temperate	11	-1.0	-0.2	0.9
NGPN	Northern Great Plains	13	0.0	0.5	2.4
ROMN	Rocky Mountain	6	0.2	0.3	2.3
SCPN	Southern Colorado Plateau	19	-0.1	0.3	1.5
SECN	Southeast Coast	17	-0.6	0.2	5.0
SFAN	San Francisco Bay Area	6	0.4	1.1	2.5
SFCN	South Florida/Caribbean	4	0.1	0.3	0.5
SIEN	Sierra Nevada	4	1.3	1.6	2.8
SODN	Sonoran Desert	11	0.1	0.4	1.7
SOPN	Southern Plains	10	-0.3	0.3	2.1
UCBN	Upper Columbia Basin	8	0.1	0.5	5.7

Table 8. Distribution of estimated change from 2001 to 2011 in total inorganic nitrogen deposition across I&M parks in each of the park networks in the conterminous United States, derived by the Total Deposition project (Schwede and Lear 2014). Deposition estimates are based on three-year averages centered on the years 2001 and 2011.

Network Code	Network Name	Number of Parks	Changes in Deposition (kg N/ha/yr)		
			Minimum	Median	Maximum
APHN	Appalachian Highlands	4	-2.2	-1.8	-0.8
CHDN	Chihuahuan Desert	6	-0.8	-0.5	0.0
CUPN	Cumberland Piedmont	14	-2.9	-1.8	1.7
ERMN	Eastern Rivers and Mountains	9	-4.5	-3.5	-2.7
GLKN	Great Lakes	9	-3.5	-1.4	0.5
GRYN	Greater Yellowstone	3	-0.2	0.4	0.6
GULN	Gulf Coast	8	-5.3	-1.2	-0.1
HTLN	Heartland	15	-3.5	0.6	5.0
KLMN	Klamath	6	-0.7	0.2	0.4
MEDN	Mediterranean Coast	3	-4.3	-1.2	0.2
MIDN	Mid Atlantic	10	-5.1	-2.9	-0.8
MOJN	Mojave Desert	6	-0.8	0.0	0.6
NCBN	Northeast Coastal and Barrier	8	-8.0	-2.1	5.6
NCCN	North Coast and Cascades	7	-0.9	-0.2	1.4
NCPN	Northern Colorado Plateau	16	-0.8	0.0	2.2
NCRN	National Capital Region	11	-4.4	-2.6	0.5
NETN	Northeast Temperate	11	-6.3	-3.2	-1.3
NGPN	Northern Great Plains	13	-0.8	0.0	1.8
ROMN	Rocky Mountain	6	-0.3	0.1	1.7
SCPN	Southern Colorado Plateau	19	-1.4	0.1	1.7
SECN	Southeast Coast	17	-6.9	-2.2	2.1
SFAN	San Francisco Bay Area	6	-7.3	-1.4	1.9
SFCN	South Florida/Caribbean	4	-2.1	-1.9	-0.6
SIEN	Sierra Nevada	4	1.4	1.4	2.8
SODN	Sonoran Desert	11	-0.4	0.1	1.6
SOPN	Southern Plains	10	-1.5	-0.5	1.0
UCBN	Upper Columbia Basin	8	-0.1	0.4	5.4

Effects of Air Pollutants

Air pollutants, both ambient aerosols and deposited materials, contribute to a range of environmental stressors in the national parks. Each stressor has the potential to cause one to many effects on sensitive receptors (Table 9), and effects will depend on both the type and amount of pollutant and the inherent sensitivity of the receptor or ecosystem. Background information on each type of ecosystem stress is discussed in the sections that follow.

Table 9. Matrix of environmental stressors and selected effects caused by air pollutants.

Pollutant	Stressor	Selected Effects
Acidic deposition	Soil acidification	Decreased soil base saturation; loss of plant nutrients; increased stress to sensitive plants and loss of sensitive terrestrial species
	Surface water acidification	Decreased surface water ANC and pH; increased stress to sensitive aquatic biota and loss of sensitive aquatic species.
Ground level ozone	Ozone exposure to plant foliage	Increased stress to ozone-sensitive plants, reduced growth, foliar injury
Nutrient N deposition	Nutrient enrichment	Eutrophication, changes in species composition, loss of biodiversity
Toxic substances	Exposure to toxic conditions	Bioaccumulation of toxic materials, neurotoxicity, reproductive effects
Atmospheric concentrations of SO_4^{2-} and NO_3^-	Formation of haze	Visibility degradation

Acidification

Atmospheric deposition of S and/or N can cause acidification of soil, soil water, lakes, and streams. In most portions of the United States that have experienced soil and water acidification attributable to air pollution, such effects have mainly been due to S inputs. There are, however, some regions, especially in the western United States, where resources are more threatened or have been more affected by the acidity of N inputs than by the acidity of S inputs. This is at least partially due to the low levels of S deposition received at most western locations. There are also regions where both atmospheric S and N contribute substantially to the observed acidification. These include portions of the Northeast, West Virginia, and high elevations in North Carolina and Tennessee. Historically these areas received more S than N deposition, but now receive about equal amounts.

The fresh water aquatic ecosystems within the national parks that are thought to be most sensitive to the effects of acidification from atmospheric S and N deposition include remote lakes which often occur at high elevation, and headwater (Strahler order 1-3) streams. Acid-sensitive waters most

commonly occur in areas of high elevation and steep terrain, on shallow soils and bedrock types that provide limited contribution of base cations to drainage water.

The soils that are thought to be most sensitive to acidification effects include shallow soils having low base saturation (BS; less than about 12%). These low-BS soils generally exhibit low weathering rates and tend to have low clay content. They are often found at high elevation and are exposed to relatively high levels of precipitation, which can leach nutrient base cations to drainage water, further reducing the soil's ability to neutralize acidity from acidic deposition

Terrestrial Effects

Acidification can affect soils and vegetation. Acidification can deplete soil nutrients and release metals toxic to plant roots. Two tree species (red spruce [*Picea rubens*] and sugar maple [*Acer saccharum*]) are known to be highly susceptible to damage from acidic deposition. Some national parks have extensive coverage of vegetation types that include one or both of these sensitive tree species. Other national parks are dominated by other forest vegetation or some other cover type thought to be less sensitive to such effects at S and N deposition levels that are commonly found in the United States. Although acidification effects in the United States are expected to be especially pronounced in the plant communities that include these tree species, the same kinds of effects might also occur in other vegetation types. Nevertheless, effects of acidification on vascular plant species other than red spruce and sugar maple have been inferred based on gradient studies (cf., Thomas et al. 2010), but are poorly documented in this country.

Many lichen species are known to be especially sensitive to air pollution. Effects seem to be more clearly associated with N inputs than with S inputs (Bobbink et al. 2003, Geiser and Neitlich 2007, Glavich and Geiser 2008). These effects may be driven by nutrient enrichment processes more than acidification processes. It is also likely, however, that S air pollution has impacted the distribution of lichens, especially in the eastern United States, but there are few broad regional or national data available to evaluate that.

The release of base cations from the soil into soil water through weathering, cation exchange, and mineralization contributes to neutralization of acidity derived from acidic deposition and/or natural processes (van Breemen et al. 1983). If the acidity is associated with anions that are mobile within the soil environment, such as SO_4^{2-} and NO_3^- at some locations, cations can be leached into ground waters and eventually to surface waters. Some loss of base cations from soil is a natural process. The limited mobility of anions associated with naturally derived organic acids and carbonic acid controls the rate of base cation leaching under conditions of low atmospheric deposition of S and N. Because inputs of S and N in acidic deposition supply anions that are often (but not always) highly mobile in the soil, these mineral acid anions accelerate base cation leaching (Cronan et al. 1978). Depletion of nutrient base cations, especially Ca, can cause damage to acid-sensitive plants and those that require high Ca levels.

In regions of the eastern United States affected by acidic deposition, the total concentration of mineral acid anions in soil waters and surface waters (mainly SO_4^{2-}) has changed from historical conditions. In response to these changes in SO_4^{2-} concentration, the concentrations of other ions in

surface water must also have changed to maintain electroneutrality. The leaching of SO_4^{2-} does not directly cause environmental effects. Rather, the changes in other ions are responsible for environmental effects of drainage water acidification. As SO_4^{2-} concentration increased over time during the 20th century, other anions (mainly bicarbonate [HCO_3^-], or organic acid anions) must have decreased and/or cations (e.g., base cations, hydrogen ion [H^+], or inorganic monomeric Al [Al_i]) must have increased in solution to maintain the charge balance whereby the sum of the cations equals the sum of the anions. Changes in the concentration of these ions have affected the ability of soils to support sensitive plant species.

Most acidification effects on plants are mediated through the soil, and are governed by Al toxicity and nutrient base cation (Ca, Mg, K) deficiencies. Nitrogen saturation can also be involved. These three factors are often closely related. Each is discussed below.

Aluminum Toxicity

One of the key biogeochemical processes that is altered by acidic deposition is the mobilization of Al from soils to waters (Cronan and Schofield 1979, Mason and Seip 1985), causing potential toxic impacts to both terrestrial and aquatic organisms. Aluminum solubility increases at pH values below about 5.5. Aluminum concentrations in drainage waters having pH below about 5.0 are often substantially higher than in waters having pH above 6.0. At high concentration in soil water, Al is toxic to plant roots. Plants affected by high Al concentration in soil water may show reduced root growth. This limits the ability of the plant to take up water and nutrients, especially Ca (Parker et al. 1989).

Red spruce trees died over large portions of the eastern United States in the 1980s. This mortality was linked to exposure of foliage to acidic cloud water and to an increase in the amount of dissolved Al compared with dissolved Ca^{2+} in soil water. Some of the red spruce decline occurred at high-elevation sites which frequently experience cloud cover.

The leaching of atmospherically deposited SO_4^{2-} into soil waters, and eventually to surface waters, is an important mechanism controlling soil acidification and Al toxicity to plants at most acid-impacted areas in the eastern United States. At such locations, much of the deposited S is leached to surface waters as SO_4^{2-}, which contributes to soil and surface water acidification and Al mobilization. In contrast, much of the deposited N is taken up from watershed soils by plants at many such locations, reducing its acidification potential. Thus, the mobilization and toxicity of Al are largely controlled by SO_4^{2-} mobility in most affected ecosystems. Nitrate mobility is also important in some locations, but the dominant mobile strong acid anion in U.S. national parks is usually SO_4^{2-}.

Depletion of Base Cations from Soil

Base cations, some of which are necessary plant nutrients, are common in rocks and soils, but largely in forms that are unavailable to plants. There is also a pool of bioavailable exchangeable base cations that are adsorbed to negatively charged surfaces of soil particles. Base cations in this pool are gradually leached from the soil in drainage water, but are constantly resupplied through weathering and atmospheric deposition of base cations. Weathering slowly breaks down rocks and minerals, releasing base cations to the pool of adsorbed exchangeable base cations on the soil. The balance

between base cation supply and base cation loss determines whether the pool of available base cations is increasing or decreasing in size over time. Enhanced leaching of base cations by acidic deposition in some cases can deplete the soil of exchangeable bases faster than they are resupplied (Cowling and Dochinger 1980). Nutrient base cations, including Ca^{2+}, Mg^{2+}, and K^{+}, are taken up through plant roots from the soil water to satisfy plant nutritional needs. In soils having low base saturation, exchangeable Ca^{2+}, Mg^{2+}, or K^{+} can be depleted so much that nutrient deficiencies develop in vegetation.

The hardwood tree species most commonly associated with acidification effects is sugar maple. It is distributed throughout the northeastern United States, the Upper Midwest, and central Appalachian Mountain region as a component of the northern hardwood forest. Several studies, mainly in Pennsylvania and New York, have indicated that sugar maple decline is linked to the occurrence of relatively high levels of acidic deposition and base-poor soils. It results, in part, from Ca depletion.

The health of sugar maple trees is strongly influenced by the availability of Ca and other base cations in soil. Trees that grow on soils having low base cation supply are stressed and consequently often become more susceptible to damage from defoliating insects, drought, and extreme weather. The overall response includes death of mature trees and poor regeneration of seedlings.

Soil acidification and depletion of soil base cations may be contributing to sugar maple mortality, especially on sites having marginal soils. Sugar maple dieback at 19 sites in northwestern and north-central Pennsylvania and southwestern New York was correlated with combined stress from defoliation and soil deficiencies of Mg and Ca (Horsley et al. 1999) . Dieback occurred predominately on ridgetops and on upper slopes, where soil base cation availability was much lower than on middle and lower slopes (Bailey et al. 1999). Sugar maple in the Adirondack Mountains of New York exhibited essentially no regeneration on sites having upper B soil horizon BS less than about 12% (Sullivan et al. 2013).

Aquatic Effects

Surface water acidification entails a decrease in acid neutralizing capacity (ANC), usually a decrease in pH, and often an increase in the concentration of Al_i in lakes and streams. Many species of aquatic biota are sensitive to water acidification, including some species of fish, invertebrates, and phytoplankton.

ANC is the most widely used water chemistry indicator for both acidic deposition sensitivity and effects. It can be measured in the laboratory by Gran titration or defined as the difference between the measured base cation and mineral acid anion concentrations in water:

$$ANC = (Ca^{2+} + Mg^{2+} + K^{+} + Na^{+} + NH_4^{+}) - (SO_4^{2-} + NO_3^{-} + Cl^{-}) \quad (1)$$

Surface water ANC reflects the end result of all of the chemical, physical, and biological interactions that occur as atmospheric deposition and precipitation move from the atmosphere into the soil and eventually emerge as drainage water in a stream or lake. ANC reflects the relative balance between base cations and strong acid anions in solution. If the sum of the base cation concentrations (in equivalence units) exceeds those of the strong acid anions, the water will have positive ANC. To the

extent that the base cation sum exceeds the strong acid anion sum, the ANC will be higher. Higher ANC is generally associated with higher pH and Ca^{2+} concentration; lower ANC is generally associated with higher H^+ and Al concentrations and a greater likelihood of toxicity to aquatic biota.

ANC levels were grouped by Cosby et al. (2006) into five major classes: Acute Concern (less than 0 μeq/L), Severe Concern (0 to 20 μeq/L), Elevated Concern (20 to 50 μeq/L), Moderate Concern (50 to 100 μeq/L), and Low Concern (greater than 100 μeq/L), with each range representing a probability of ecological damage to the aquatic community. Biota are generally not harmed when ANC values are above 100 μeq/L (U.S. EPA 2009). In acid-sensitive regions, many surface waters commonly have ANC below 100 μeq/L, and in some cases below 50 μeq/L, even in the absence of acidic deposition. Thus, although acidic deposition is responsible for loss of ANC in many sensitive waterbodies, a relatively low ANC value does not necessarily indicate that human-caused acidification has occurred.

A number of factors influence the sensitivity of aquatic ecosystems to acidification in response to S and N deposition. In particular, the geologic composition, which largely determines the base cation availability, of a region plays a dominant role in influencing the sensitivity of surface waters to the effects of acidic deposition. Bedrock geology formed the basis for a national map of surface water sensitivity (Norton et al. 1982) and has been used in numerous acidification studies of more limited extent (e.g., Bricker and Rice 1989, Dise 1984, Sullivan et al. 2007). Most of the major concentrations of low-ANC surface waters are located in areas of the United States that are underlain by bedrock resistant to weathering, with consequent low supply of base cations (U.S. EPA 2008).

Soil chemistry, land use, watershed slope, and hydrologic flowpath also contribute to the sensitivity of surface waters to acidic deposition. Land disturbance and consequent exposure of S-bearing minerals to oxidation, loss of base cations through erosion and timber harvesting, and change in N status of the forest through timber management can all influence the relative availability of mobile mineral acid anions (SO_4^{2-}, NO_3^-) and base cations (Ca^{2+}, Mg^{2+}, K^+, Na^+) in drainage water, thereby affecting the ANC of drainage water.

Effects on lakes and streams are strongly influenced by hydrology and the flowpath of water through the terrestrial watershed. The depth and chemical composition of soils, talus, and colluvium (sediment) and the slope of the watershed help to determine the residence time of subsurface water within the watershed, extent to which snowmelt and rainfall runoff interact with soils and geologic materials, and consequently the extent of NO_3^- leaching, base cation mobilization, and acid neutralization that will occur within the watershed (Sullivan 2000, Turner et al. 1990). Surface waters can have different sensitivities to acidification depending on subsurface water flow paths (Chen et al. 1984, Driscoll et al. 1991, Eilers et al. 1983). Natural hydrologic events also alter acidification and neutralization processes during snowmelt and change flowpaths during extended droughts (Webster et al. 1990).

Most watersheds in the eastern United States are not exhibiting much ANC and pH recovery of drainage water in response to recent large decreases in atmospheric S deposition due to

implementation of emissions control programs under the CAA and its amendments (Burns et al. 2011). This limited recovery is partly due to leaching loss of base cations in surface waters.

Regions of the United States that contain appreciable numbers of lakes and streams with low ANC (less than about 50 to 100 μeq/L) include portions of the Northeast (New England and the Adirondack and Catskill mountains), the Southeast (the Appalachian Mountains and portions of northern Florida), the Upper Midwest, and mountainous portions of the western United States (Charles 1991). In particular, the Adirondack and Appalachian mountains, and to a lesser extent the Upper Midwest, include many acidified surface waters that have been impacted by acidic deposition. Portions of northern Florida also contain many acidic and low-ANC lakes and streams, although the role of acidic deposition in these areas is less clear. Some of these waters may have been naturally acidic; others may have been acidified by hydrological changes associated with drawdown of the local aquifer to support agriculture and other water usage. The western United States contains many of the surface waters most susceptible to potential acidification effects, but the levels of acidic deposition in the West are relatively low in most areas, acidic surface waters are rare, and the extent of chronic surface water acidification that has occurred to date has probably been limited (U.S. EPA 2008).

High-elevation lakes and streams are of particular interest with respect to potential impacts attributable to acidic deposition. Many waters at high-elevation tend to be dilute, and this contributes to increased risk of acidification and biological change from acid input. Because soils at high elevation are often shallow and poorly developed, with much exposed bedrock, the supply of base cations with which to neutralize acidity can be low.

Spatial Patterns in Acidification Risk

Sullivan et al. (2011b) reported results of a screening study to evaluate the exposure of I&M parks and networks to acidifying atmospheric deposition and associated resource sensitivities to acidification damage. Acidification can occur in both terrestrial (soil and soil water) and aquatic (fresh surface water) ecosystems. The addition of S and N from air pollution sources to national park ecosystems can acidify soil and water and thereby alter plant, animal, fungal, and algal communities at all trophic levels. The response is driven by both the amount of air pollutants deposited and the sensitivity of the receptors on which the pollutants are deposited or to which the deposited pollutants are transported.

The assessment by Sullivan et al. (2011b) was a coarse screening study. It included consideration of three themes that influence acidification risk to park resources from atmospheric S and N deposition: acid Pollutant Exposure, inherent Ecosystem Sensitivity to acidification, and Park Protection mandates. National parks and networks were ranked according to each of these themes. A Summary Acidification Risk ranking was calculated for each park and network based on averages of the three theme rankings. A high risk ranking suggests the possibility of enhanced pollution level and/or sensitivity. In some cases, available site-specific data for particular parks or networks do not support the risk ranking. In such cases, the site-specific data are assumed to be more reflective of actual conditions.

Acid Pollutant Exposure

Acid Pollutant exposure was estimated by Sullivan et al. (2011b) in multiple variables that reflect emissions and deposition of acidifying S and N now and in the future. The amounts of S and N emitted into the atmosphere vary across the United States, generally with highest emissions associated with electricity generating power plants; major population centers; and centers of energy, agricultural, and industrial development. The direction of atmospheric transport and distance traveled vary with chemical and meteorological conditions encountered along the path from emissions source to the location at which pollutants are deposited from the air to the ground surface. Rankings were based in part on proximity of parks to known emissions point sources and to urban and agricultural areas.

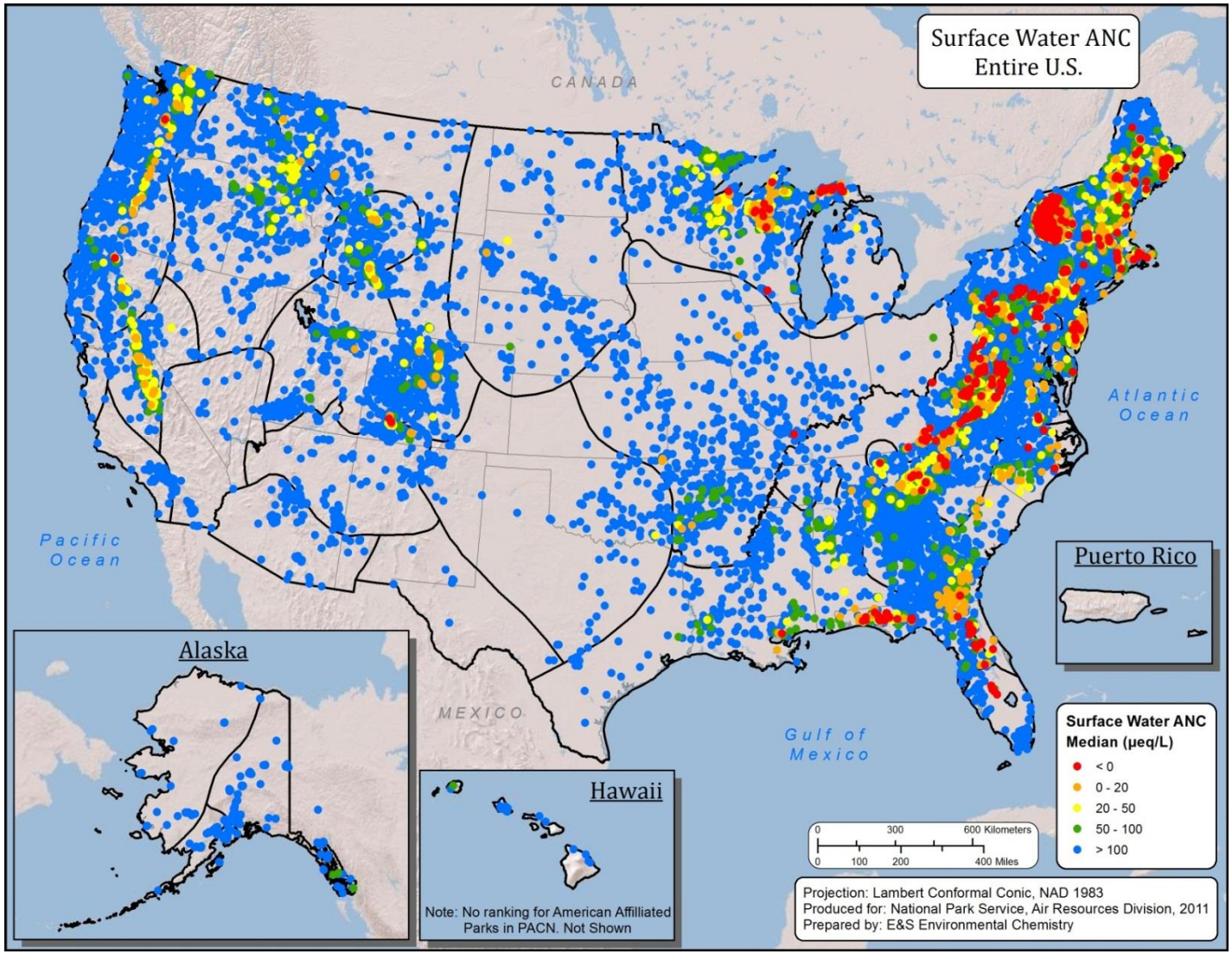
Emissions inventories are only approximations and are less certain for reduced N, as compared with S and oxidized N. Deposition estimates are also uncertain, especially for the dry component of deposition. Cloud and fog deposition have not been estimated regionally, but can be important at some locations. Estimates of wet plus dry deposition constructed by Sullivan et al. (2011b) were relatively coarse (12-km grid cells in the East; 36-km grid cells in the West) and could not fully capture spatial variation in areas of complex terrain. Nevertheless, they do provide a reasonable approximation of national and regional patterns in total acidic deposition that potentially impact the ecosystems on which this deposition falls.

Ecosystem Sensitivity to Acidification

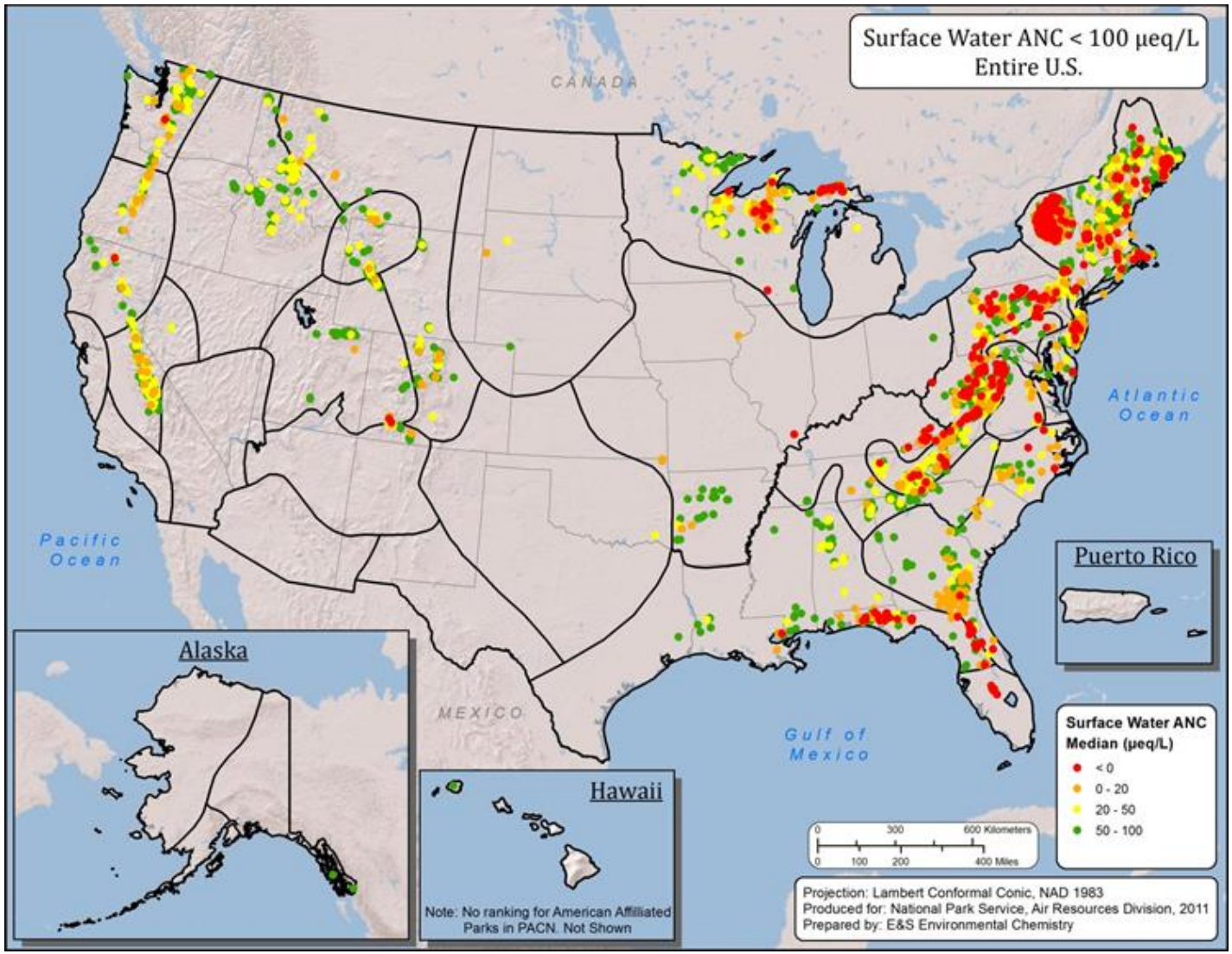
Streams and lakes vary in their sensitivity to acidification from acidic deposition. The surface waters that tend to be most sensitive to acidification are located on geological formations that contribute minimal quantities of base cations to drainage water. Acid-sensitive waters are often located at relatively high elevation, on steep slopes having shallow, base-poor soils. Maps 14a and 14b show the locations of lakes and streams in the United States known to have low ANC. These maps were compiled from available data sets and include a total of 31,662 sampling locations. Surface waters having ANC $\leq$ 50 μeq/L are considered to be especially sensitive to acidification.

Some kinds of plants appear to be more sensitive to acidification effects than others. Among the vascular plants, red spruce and sugar maple trees are known to be particularly sensitive. Their presence in the national park lands was assumed here to contribute to park sensitivity to acidification. Although other plant species are undoubtedly also highly sensitive, quantitative dose-response data are generally lacking.

Sullivan et al. (2011b) calculated the extent and distribution of the aquatic fresh water and terrestrial ecosystems within the national parks that are thought to be most sensitive to the effects of acidification from atmospheric S and N deposition. These included remote lakes which often occur at high elevation, headwater streams, base-poor soils, and red spruce and sugar maple trees.



Map 14a. Surface water ANC map, based on data compiled from the data sources listed in Table 10.



Map 14b. Surface water ANC map, shown as a subset of data represented in Map 14a, but only showing sites having median ANC ≤ 100 µeq/L.

Table 10. Data sources for national map of surface water ANC.

Database	Acronym	Source
Adirondack Lakes Survey	ALS	Adirondack Lakes Survey Corporation
Long Term Monitoring Project	LTM	U.S. EPA
Temporally Integrated Monitoring of Ecosystems	TIME	U.S. EPA
Western Adirondack Stream Survey	WASS	USGS
Eastern Lakes Survey	ELS	U.S. EPA
Western Lakes Survey	WLS	U.S. EPA
Environment Monitoring and Assessment Project	EMAP	U.S. EPA
Mid-Atlantic Streams Survey	MAHA	U.S. EPA
National Lakes Survey	NLS	U.S. EPA
Wadeable Streams Assessment	WSA	U.S. EPA
National Stream Survey	NSS	U.S. EPA
STORET	STORET	U.S. EPA
Regional EMAP	REMAP	U.S. EPA
High Elevation Lake Monitoring Program, ME	HELM	Steve Kahl, Jason Lynch
Aquifer Lakes Project, ME	ALPS	Steve Kahl, Jason Lynch
Water Quality Monitoring in George Washington and Jefferson National Forests	USFS_GWJ	USFS
Federal Land Manager Environmental Database	USFS-Database	USFS
Monongahela N.F. Database	USFS_M	USFS
North Carolina NF Database	USFS_NC	USFS
National Water Information System	USGS-1	USGS
Alpine Hydrology Research Group	AHRG	USGS
Virginia Trout Stream Sensitivity Study	VTSSS	University of Virginia

Network and Park Acidification Rankings

Networks were ranked for each emissions or deposition variable that was available spatially, from the network showing the lowest acid Pollutant Exposure (lowest rank) to the network showing the highest acid Pollutant Exposure (highest rank). These variable-specific rankings were then averaged to yield an overall acid Pollutant Exposure ranking for each of the 32 networks, where lower

numbers (near 1) reflect lower acid Pollutant Exposure and higher numbers (near 32) reflect higher acid Pollutant Exposure.

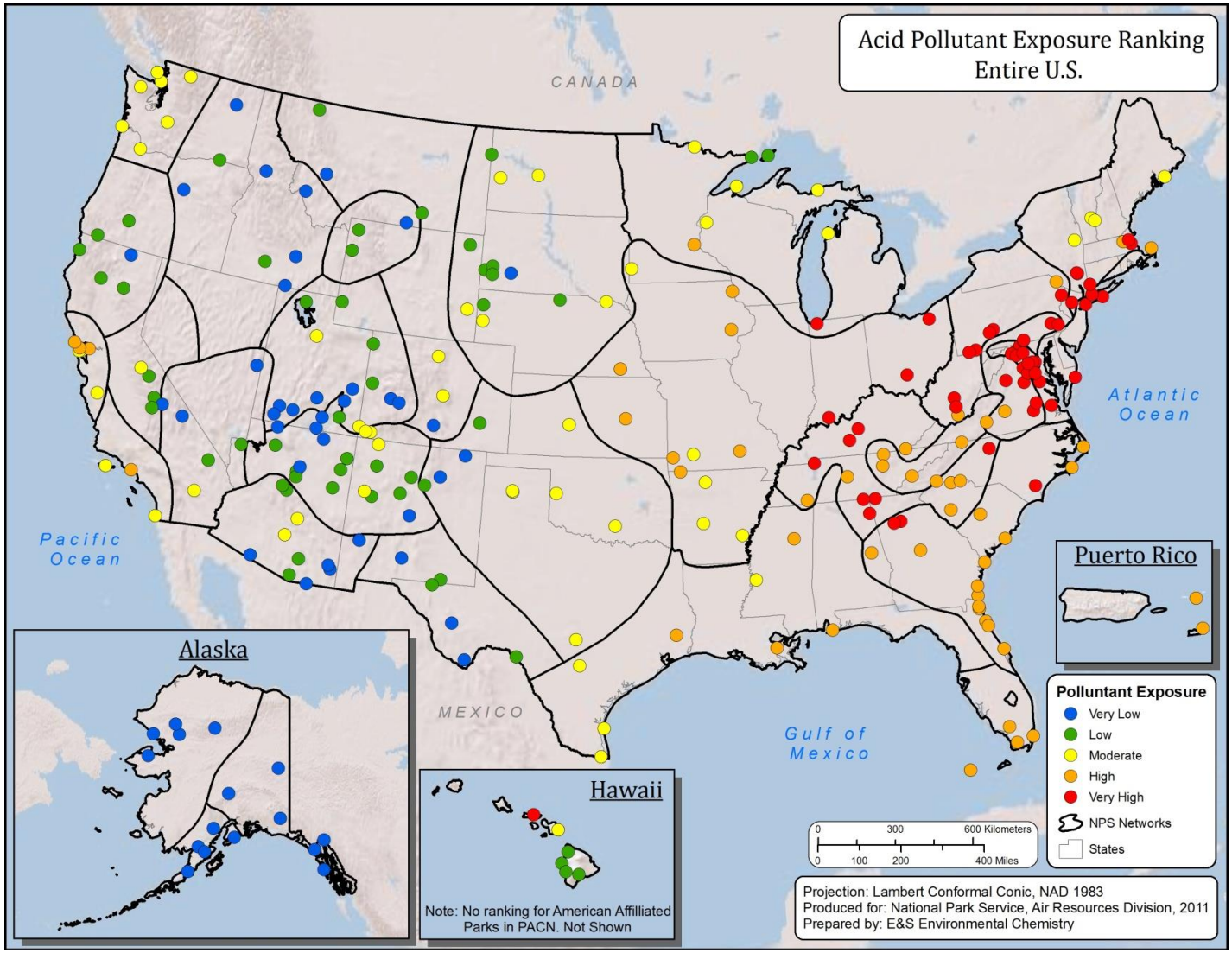
Network rankings were calculated in the same manner for the other two acidification themes: Ecosystem Sensitivity to acidification and level of Park Protection. A key element of the Ecosystem Sensitivity ranking was the location of parks within geographic areas known to be sensitive to soil and water acidification. This variable was constructed based on spatial coverages of acid sensitive resources compiled by Omernik and Powers (1983), Stoddard et al. (2003), and Sullivan et al. (2007). Ecosystem Sensitivity to acidification was also represented in part by the coverage of vegetative types expected to contain red spruce and/or sugar maple, the two tree species thought to be most sensitive to acidification and also by the abundance of high-elevation lakes and streams and low-order (1-3) streams that might be especially prone to acidification. Park Protection was represented by designation as wilderness and Class I areas to differentiate those parks specifically given a high level of protection from air pollution by the CAA or the Wilderness Act. Finally, an overall risk of acidification effects was calculated as the average of the rankings for the three themes discussed above.

As for the network rankings, park rankings were calculated individually for acid Pollutant Exposure, Ecosystem Sensitivity to acidification, and Park Protection metrics. An overall Summary Acidification Risk ranking was calculated for each I&M park.

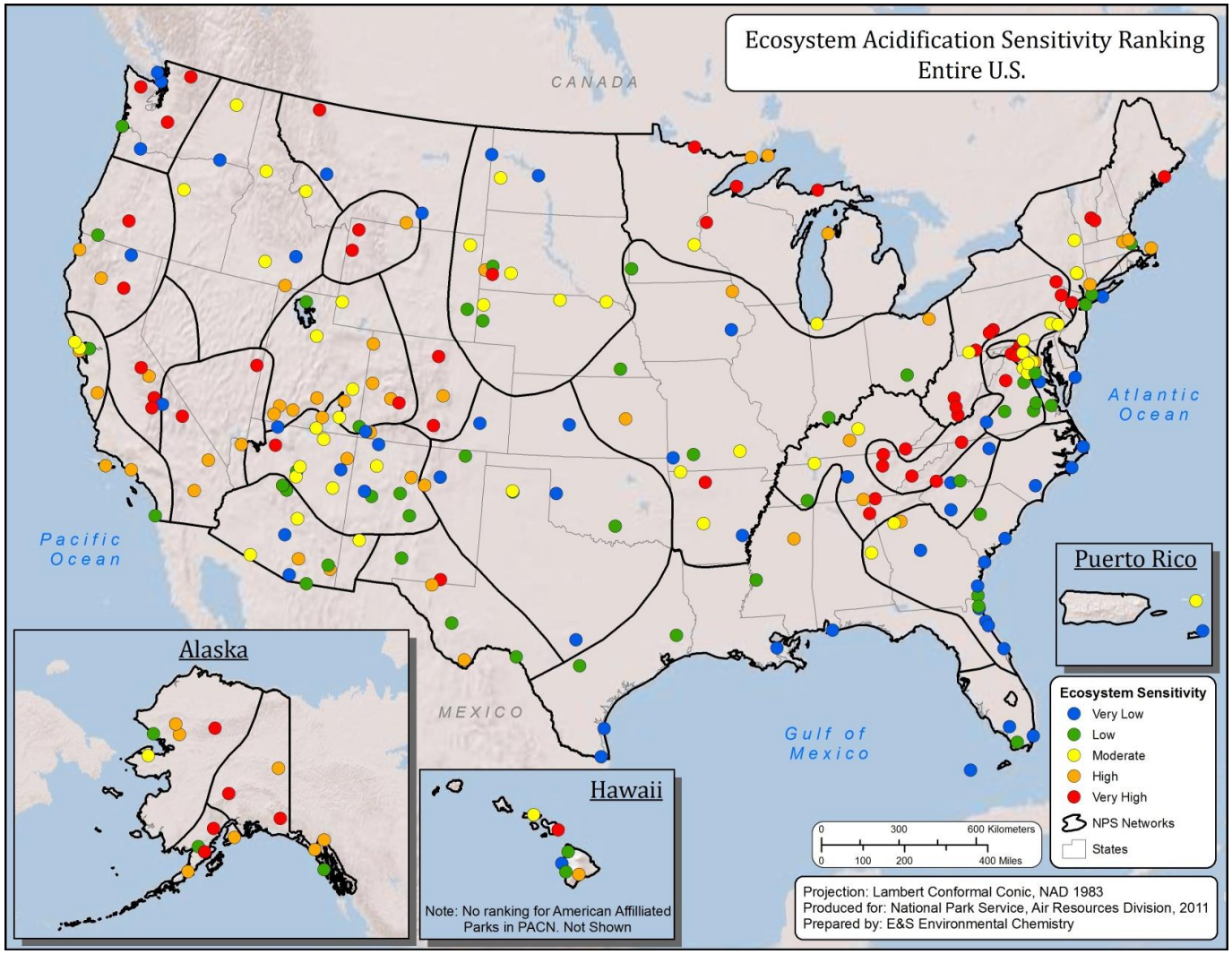
The networks that had the highest calculated Summary Acidification Risk included two western mountain networks (North Coast and Cascades, and Sierra Nevada), and one eastern network (Mid-Atlantic). Eleven of the larger (greater than 100 square miles in area) individual parks were ranked as having Very High overall risk of acidification. These included five eastern parks (Shenandoah [SHEN], GRSM, Blue Ridge [BLRI], DEWA, and New River Gorge [NERI]); five western mountain parks (Mount Rainier [MORA], North Cascades [NOCA], Olympic [OLYM], ROMO, YOSE); and one park in the Upper Midwest (Voyageurs [VOYA]).

The acidification risk rankings developed by Sullivan et al. (2011b) and used as part of the basis for assessing acidification risk here should be considered as coarse first approximations of true risk. Where survey and monitoring data are available, the measured data likely provide a more accurate indication of true sensitivity and pollution exposure than the rankings provided by Sullivan et al. (2011b). Confidence in the rankings may increase as scientific knowledge regarding acid Pollutant Exposure and inherent Ecosystem Sensitivity to acidification improve, and also as national-scale datasets that shed light on these issues become available and are depicted at finer scales.

Two of the ranking metrics developed by Sullivan et al. (2011b) are used here as screening tools to evaluate national patterns in acidification risk among the I&M parks. These are the park-specific acid Pollutant Exposure ranking (Map 15) and the park-specific inherent Ecosystem Sensitivity to acidification ranking (Map 16). These two rankings are used to identify the parks, and associated networks, that may be of greatest concern with respect to potential acidification damage.



Map 15. Park-specific rankings of I&M parks with respect to acid Pollutant Exposure. (Source: Sullivan et al. 2011b)



Map 16. Park-specific rankings of I&M parks with respect to inherent Ecosystem Sensitivity to acidification. (Source: Sullivan et al. 2011b)

Spatial Patterns in Surface Water ANC

National and regional databases of measured water chemistry data were aggregated for this assessment to generate a master database to represent surface water ANC status throughout the NPS networks. Sources of data were mostly U.S. federal agencies (Table 10). Duplicate records among the data sources were identified and removed. An attempt was made to also remove samples expected to be affected by acid mine drainage, sea salt spray and road salt application. This was performed by applying chemistry screens which removed samples with observed Cl^- or SO_4^{2-} greater than 300 µeq/L or ANC < -100 µeq/L. These samples were considered to represent ANC results that were likely confounded by disturbances other than acidic deposition.

The final database contained 196,997 ANC values from 19,808 spatially unique sites sampled between 1/8/1980 and 5/25/2011 (Map 14a). There were 6,065 sites with low (< 100 µeq/L) median ANC derived from 69,649 samples (Map 14b). The distribution of surface water ANC across the NPS networks is shown in Table 11. Although these data cannot be considered to be statistically representative of spatial distributions of surface water ANC across the nation, there are clear patterns that emerge. Acidic (ANC ≤ 0 µeq/L) lakes and streams are widely distributed, but are mostly confined to upstate New York, the Appalachian Mountains, New England, the Upper Midwest, and Florida. Low-ANC lakes and streams (0-100 µeq/L) occur in these same areas plus portions of Arkansas, the Gulf states, and the Rocky, Cascade, and Sierra Nevada mountains. In other regions of the United States, available water quality data are indicative of well-buffered streams and lakes that are likely to be insensitive to acidic deposition.

Nutrient Nitrogen Enrichment

Nutrient enrichment describes a host of environmental changes that can occur when the availability of a key nutrient is increased as a consequence of air or water pollution. Most of the nutrients required for tree growth are generally supplied through internal ecosystem processes, including decomposition. Nutrient enrichment effects can occur in terrestrial, wetland, and aquatic environments. In all cases, the addition of a key nutrient (N) from atmospheric deposition can contribute to changes in the species mix of the plant, fungal, and algal communities. Nutrient enrichment can cause some species to thrive, at the expense of others. Thus, the mix of species present in an ecosystem can change as a consequence of nutrient addition.

Table 11. Distribution of measured surface water ANC (µeq/L) values across the NPS networks. Data are based on samples mapped in Map 14a, arranged in order of increasing median ANC.

Network Name	Unit Code	Number of Sites	Minimum	5th Percentile	25th Percentile	Median	75th Percentile	95th Percentile	Maximum
Northeast Temperate	NETN	4300	-96.7	-23.1	12.8	80.0	199.0	853.6	6580.0
Northeast Coastal and Barrier	NCBN	349	-71.4	-2.2	20.0	100.0	280.0	911.7	3600.0
Appalachian Highlands	APHN	1597	-22.0	2.0	43.0	106.0	228.7	1477.6	5602.2
Sierra Nevada	SIEN	518	0.4	21.6	45.0	106.6	388.6	1380.5	4340.0
Eastern Rivers and Mountains	ERMN	1636	-99.7	-23.7	64.5	194.9	500.0	1805.0	5792.2
Mid Atlantic	MIDN	834	-85.3	-10.4	77.7	220.0	539.0	1620.5	5020.0
Cumberland Piedmont	CUPN	886	-20.4	16.8	132.8	340.0	1120.0	2754.9	4340.0
Gulf Coast	GULN	693	-58.7	0.0	120.0	368.0	910.0	2596.0	5200.0
Southeast Coast	SECN	1103	-87.0	20.0	200.0	370.0	550.0	1100.0	3810.0
National Capital Region	NCRN	89	6.9	83.6	220.0	391.0	895.0	2455.4	3560.0
Great Lakes	GLKN	1103	-48.6	7.0	81.5	391.5	1696.8	3738.0	6040.0
Southwest Alaska	SWAN	64	140.0	147.5	260.0	410.0	560.0	797.0	940.0
Pacific Island	PACN	23	80.0	132.0	370.0	420.0	540.0	984.0	1040.0
North Coast and Cascades	NCCN	815	-4.7	30.9	183.3	496.5	1005.0	2140.0	5844.9
Upper Columbia Basin	UCBN	887	20.9	44.2	122.8	518.0	1320.0	3266.3	18720.0
Greater Yellowstone	GRYN	495	12.0	35.4	88.8	518.2	1523.4	3860.0	6280.0
Klamath	KLMN	599	0.0	26.7	219.1	654.6	1217.2	2862.0	8004.9
Rocky Mountain	ROMN	1186	5.0	42.2	200.9	744.6	1817.5	4305.0	10700.0
Southeast Alaska	SEAN	52	60.0	173.0	512.5	920.0	1375.0	3209.0	15180.0

Table 11 (continued). Distribution of measured surface water ANC (µeq/L) values across the NPS networks. Data are based on samples mapped in Map 14a, arranged in order of increasing median ANC.

Network Name	Unit Code	Number of Sites	Minimum	5th Percentile	25th Percentile	Median	75th Percentile	95th Percentile	Maximum
Central Alaska	CAKN	85	260.0	360.0	670.0	960.0	2360.0	3924.0	5200.0
Northern Colorado Plateau	NCPN	788	-5.7	59.3	138.3	1173.7	3400.0	6012.5	12020.0
Arctic	ARCN	40	310.0	716.0	985.0	1300.0	1625.0	2143.5	3300.0
Southern Colorado Plateau	SCPN	216	10.0	48.7	484.6	1480.0	2810.0	4645.0	9847.1
Southern Plains	SOPN	140	28.9	185.8	648.4	1500.0	2713.8	4790.0	14200.0
Heartland	HTLN	637	0.0	100.0	524.5	1652.2	2860.0	4920.0	6520.0
Mojave Desert	MOJN	86	126.9	476.4	955.0	2000.0	3775.0	4548.9	5940.0
South Florida Caribbean	SFCN	108	-46.1	29.9	542.5	2050.0	2805.0	4388.0	5400.0
San Francisco Bay Area	SFAN	48	354.5	476.0	1374.6	2115.0	2535.0	3432.0	6860.0
Mediterranean Coast	MEDN	40	300.0	579.0	1492.5	2242.5	3490.0	6628.0	9540.0
Sonoran Desert	SODN	82	115.4	540.0	1047.5	2260.0	3552.5	4619.0	5922.0
Northern Great Plains	NGPN	263	20.0	786.0	2149.0	3040.0	4686.7	9798.0	14400.0
Chihuahuan Desert	CHDN	9	740.0	1396.0	2480.0	3320.0	3840.0	8712.0	11920.0

Some fresh water aquatic, wetland, and terrestrial ecosystems are thought to be highly sensitive to the effects of nutrient enrichment from atmospheric N deposition. These include remote lakes at high elevation, and also alpine, arctic herbaceous, meadow, arid, and semi-arid terrestrial ecosystems, and wetland ecosystems. Some national parks have extensive coverage of one or more of these presumed highly sensitive ecosystem types. Other national parks are dominated by forest vegetation or some other cover type thought to be less sensitive to such effects at N deposition levels that are commonly found in the United States. Although nutrient enrichment effects in the United States are expected to be most pronounced in these plant communities that lack trees, the same kinds of effects from modest N loading can also occur in forest communities. It is known that N fertilization can increase tree growth, at least to a point, and cause changes to forest understory vegetation, but long-term effects on forest understory plants and/or differential growth effects on different tree species are poorly known in this country. Estuaries and near-coastal marine waters can also be highly sensitive to nutrient enrichment effects from anthropogenic N. In addition to atmospheric N inputs, however, a wide variety of point and nonpoint pollution sources often contribute N to estuarine and near-coastal waters, thus complicating assessment of effects from the atmospheric contributions.

Terrestrial Effects

In many terrestrial ecosystems, N is the most important nutrient limiting the growth of plants. If an appreciable amount of N is added from atmospheric deposition, plant growth rates can increase. Because some species are better able to take advantage of added N than others, some plant species grow at the expense of others. The species that benefit are often non-native opportunistic species; those that are suppressed are sometimes rare native species.

The extent to which ecosystems respond to nutrient addition depends in part on the extent to which the growth of plants is limited by N availability, versus the availability of phosphorous (P), light, water, or some other nutrient. Most north temperate terrestrial ecosystems are at least partially N-limited. If the availability of N is increased, many of the plants will grow faster. There can be a shift in the competitive advantage to favor those plants. This can decrease species diversity, alter the species make-up of the plant community, and can eliminate some of the rare, or otherwise valued, species. In general, plant communities that are dominated by herbaceous plants appear to be more sensitive to N enrichment than plant communities dominated by woody plants. This may be partly because it takes a long time for scientists to document effects on trees, which can grow for decades or centuries. Nutrient enrichment effects on plant communities in the United States have been most convincingly demonstrated for herbaceous arctic and alpine plant communities, meadows, wetlands, and arid or semi-arid lands (U.S. EPA 2009). These are the primary plant community types that are discussed here. This does not mean that some of these same effects may not also be occurring in forest communities.

Alpine plant communities are known for their high diversity of vascular plant species (Bobbink et al. 2010) and have been shown to be especially sensitive to N enrichment. Some studies suggest that sedges benefit more from N addition to alpine herbaceous plant communities than do grasses or forbs (Bobbink et al. 2010, Bowman et al. 2006). Changes in the abundance of a species of alpine sedge (*Carex rupestris*) have been demonstrated at N deposition levels near 3 kg N/ha/yr (Bowman et al.

2012). More dramatic effects on alpine vascular plant community composition within a relatively short time period (a few years) probably require higher levels of N deposition, perhaps near 10 kg N/ha/yr (Bowman et al. 2006). Model simulations suggest that effects can develop over centuries in response to very low levels of N input (McDonnell et al. 2014, Sverdrup et al. 2012). There are a number of plant community characteristics in the alpine zone that appear to govern sensitivity to N input. These include low temperature, restricted growing season, low levels of primary production, and wide variation in moisture regimes from boggy meadows to the desiccating conditions of wind-swept ridges (Bowman et al. 1993, Bowman 1994, Bowman and Fisk 2001). Another contributing factor is the fact that soil formation is a slow process in the harsh alpine environment. Therefore, alpine plants have evolved under conditions of low nutrient supply (U.S. EPA 2008). In some alpine scrub habitats, ground layer bryophytes and lichens are thought to be especially sensitive to N addition (Britton and Fisher 2007, Fremstad et al. 2005).

Arctic plants have not been well studied with regard to their sensitivity to modest levels of N enrichment that might correspond with potential future levels of atmospheric N deposition. Nevertheless, some arctic plant communities share many commonalities with alpine vegetation and are therefore thought to be highly sensitive. Arctic environmental conditions also contribute to slow soil development and low nutrient availability, thereby enhancing sensitivity to N deposition inputs. Low levels of N addition (1-5 kg/ha/yr) have been shown to change species composition and cover of grasses, forbs, and shrubs in tundra ecosystems (Arens et al. 2008).

Increased N input has been shown to reduce plant biodiversity in grasslands in both Europe and North America (Bobbink et al. 2003, Clark and Tilman 2008, Stevens et al. 2004). Such effects have been shown across a range of soil conditions. Changes in species composition have been reported at N deposition levels as low as about 10 kg N/ha/yr (Bobbink et al. 2003). In the San Francisco Bay area, which receives total N deposition of about 10-15 kg N/ha/yr, non-native nitrophilous (N-loving) grasses have displaced native plant species. This effect has been attributed to greater N supply from the atmosphere combined with cessation of livestock grazing, which had previously removed some of the excess N from the ecosystem (Fenn et al. 2003b, U.S. EPA 2008). A survey across acidic grasslands in the United Kingdom by Stevens et al. (2004) estimated a decrease of one plant species for every 2.5 kg N/ha/yr of deposition.

Experimental N-fertilization studies have been conducted in arid and semi-arid plant communities in southern California and the Colorado Plateau. Such vegetation communities are commonly dominated by shrubs, but can also be dominated by grasses, forbs, and/or cacti. Results of the fertilization studies suggested increased biomass of some non-native plant species and reduced biomass of some native species with increased N. There also appears to be an increased fire risk where grasses replaced shrub cover. There are apparently multiple interactions involving N-stimulation of non-native grass species, competitive abilities of native forb and shrub species, and the incidence of fire (cf., Eliason and Allen 1997, Yoshida and Allen 2001). The coastal sage scrub plant community in California, in particular, has been declining for many decades. Current scientific understanding suggests that atmospheric N deposition plays a role in this decline, and causes shrub replacement by Mediterranean annual grasses, which promote increased fire cycles (D'Antonio and

Vitousek 1992, Fenn et al. 2003b, Minnich and Dezzani 1998, Padgett and Allen 1999, Padgett et al. 1999).

Additional studies have been conducted in desert plant communities, suggesting that N additions in the range of 10 kg N/ha/yr or higher can cause invasion of exotic plant species, including grasses (U.S. EPA 2008). Effects appear to be more pronounced at higher elevations, perhaps because the increased precipitation that occurs at higher elevation can contribute to increased grass production. Increased grass biomass in desert plant communities is associated with increased fire frequency (Brooks 1999, Brooks and Esque 2002, Brooks et al. 2004). Effects of N deposition on arid and semiarid plant communities may vary with moisture levels. In Joshua Tree National Park (JOTR), N loadings of 3-4 kg/ha/yr were estimated to significantly increase cover of exotic grasses, with subsequent increases in fire risk (Rao et al. 2010). In some cases, N may be limiting during wet seasons or years, whereas water may be limiting during dry seasons or years.

Lichens are typically among the most N-sensitive terrestrial receptors (Bobbink et al. 2003, Fenn et al. 2003a, Geiser et al. 2010, Vitt et al. 2003). Most lichens can be classified into groups as oligotrophic (restricted to N-poor environments), mesotrophic (require moderate N supply), and eutrophic (prefer N-rich environments). Some additional lichen taxa exhibit broad tolerance to N supply. Using the presence or abundance of such lichen indicator taxonomic groups can be problematic in regions such as southern California and much of the eastern United States because N, and in some places also S, deposition over the past 50 years or more has been so high that many of the oligotrophic lichen species have already been extirpated (Geiser et al. 2010).

Lichens that inhabit trees are called epiphytes. They tend to be highly sensitive to N inputs and are widely recognized as good early warning indicators of terrestrial ecosystem effects from atmospheric N input (Fenn et al. 2011). Epiphytic lichens vary in their N requirements. Montane species tend to be adapted to low N availability and are classified as oligotrophic. They are commonly found on coniferous trees. Valley species tend to be adapted to more mesotrophic conditions, and often occur on hardwood trees. Eutrophic species are adapted to high N supply, often in association with animal nesting or roosting sites. Atmospheric N deposition results in a shift from more oligotrophic towards more eutrophic conditions; this shift is typically accompanied by a change in the lichen community to favor the mesotrophic and eutrophic forms, with a decrease in the oligotrophic species (Geiser et al. 2010). Many lichen species that are prevalent in the western United States have relatively well known N requirements (Table 12).

A change in lichen species distribution and abundance in response to a change in N supply can have broader ecosystem-level effects. This is due to the importance of various oligotrophic lichen species as forage, for nutrient cycling, and as nesting materials for other organisms.

Table 12. List of lichen species that occur in the western United States and that have known N requirements (McCune and Geiser 2009).

Species	N Rating Class[1]	N Requirement	Peak N Deposition Frequency (kg N/ha/yr)
Ahtiana sphaerosporella	O	Low-Mod	2.0
Alectoria imshaugii	O	Low-Mod	1.9
Alectoria sarmentosa	O	Low-Mod	2.4
Alectoria vancouverensis	O	Low-Mod	2.3
Bryoria bicolor	O	Low	1.1
Bryoria capillaris	M	Mod	2.7
Bryoria fremontii	O	Low-Mod	1.9
Bryoria friabilis	M	Mod	2.6
Bryoria furcellata	O	Low	1.1
Bryoria fuscescens	O	Low-Mod	2.3
Bryoria glabra	O	Low-Mod	2.4
Bryoria pseudocapillaris	O	Low	1.1
Bryoria pseudofuscescens	O	Low-Mod	2.1
Bryoria spiralifera	O	Low	1.1
Bryoria subcana	M	Mod	3.4
Bryoria trichodes	M	Mod	2.7
Candelaria concolor	E	Hi	6.1
Cavernularia hultenii	O	Low	1.1
Cavernularia lophyrea	O	Low	1.1
Cetraria californica	O	Low	1.1
Cetraria chlorophylla	M	Mod	2.7
Cetraria merrillii	O	Low-Mod	1.9
Cetraria orbata	O	Low-Mod	2.4
Cetraria pallidula	O	Low-Mod	1.9
Cetraria platyphylla	O	Low-Mod	2.3
Cetraria subalpina	M	Mod	3.6
Cladonia bellidiflora	O	Low	1.1
Cladonia carneola	O	Low-Mod	2.0

[1] E = eutrophic; M = mesotrophic; O = oligotrophic

Table 12 (continued). List of lichen species that occur in the western United States and that have known N requirements (McCune and Geiser 2009).

Species	N Rating Class[1]	N Requirement	Peak N Deposition Frequency (kg N/ha/yr)
Cladonia chlorophaea	E	Broad	4.7
Cladonia furcata	O	Low-Mod	2.1
Cladonia macilenta	E	Hi	6.1
Cladonia norvegica	O	Low	1.1
Cladonia ochrochlora	M	Mod	2.7
Cladonia pyxidata	M	Mod	3.4
Cladonia squamosa	E	Broad	4.6
Cladonia transcendens	O	Broad	2.3
Cladonia umbricola	M	Mod	3.7
Cladonia verruculosa	O	Low-Mod	1.9
Collema nigrescens	E	Broad	6.1
Erioderma sorediatum	O	Low	1.1
Esslingeriana idahoensis	O	Low-Mod	2.0
Evernia prunastri	E	Hi	6.1
Fuscopannaria leucostictoides	M	Mod	3.6
Fuscopannaria mediterranea	M	Broad	3.2
Fuscopannaria pacifica	O	Low	1.1
Heterodermia leucomela	O	Low	1.1
Hypogymnia apinnata	O	Low-Mod	2.3
Hypogymnia duplicata	O	Low	1.1
Hypogymnia enteromorpha	O	Low-Mod	2.3
Hypogymnia heterophylla	O	Low	1.1
Hypogymnia imshaugii	O	Low-Mod	2.4
Hypogymnia inactiva	M	Mod	3.8
Hypogymnia metaphysodes	O	Low-Mod	2.4
Hypogymnia occidentalis	M	Mod	2.6
Hypogymnia oceanica	M	Mod	2.7
Hypogymnia physodes	E	Broad	4.9

[1] E = eutrophic; M = mesotrophic; O = oligotrophic

Table 12 (continued). List of lichen species that occur in the western United States and that have known N requirements (McCune and Geiser 2009).

Species	N Rating Class[1]	N Requirement	Peak N Deposition Frequency (kg N/ha/yr)
Hypogymnia rugosa	M	Mod	3.6
Hypogymnia tubulosa	M	Mod-Hi	4.3
Hypotrachyna sinuosa	O	Low	1.1
Leioderma sorediatum	O	Low	1.1
Leptogium brebissonii	O	Low	1.1
Leptogium furfuraceum	M	Mod-Hi	3.2
Leptogium gelatinosum	E	Hi	6.1
Leptogium lichenoides	O	Low	1.1
Leptogium palmatum	O	Low	1.1
Leptogium polycarpum	M	Mod	2.8
Leptogium saturninum	E	Mod-Hi	4.7
Letharia columbiana	M	Mod	3.2
Letharia vulpina	O	Low-Mod	2.0
Lichinodium canadense	O	Low-Mod	2.2
Lobaria hallii	M	Mod	3.0
Lobaria oregana	O	Low	1.1
Lobaria pulmonaria	O	Low-Mod	2.2
Lobaria scrobiculata	M	Mod	3.2
Melanelixia fuliginosa	E	Hi	6.1
Melanelixia glabra	M	Mod-Hi	3.3
Melanelixia subaurifera	E	Hi	6.1
Melanohalea elegantula	E	Mod-Hi	5.0
Melanohalea exasperatula	M	Mod-Hi	3.2
Melanohalea subelegantula	E	Hi	6.1
Melanohalea subolivacea	M	Mod	3.3
Menegazzia terebrata	O	Low	1.1
Nephroma bellum	O	Low	1.1
Nephroma helveticum	O	Low-Mod	2.4

[1] E = eutrophic; M = mesotrophic; O = oligotrophic

Table 12 (continued). List of lichen species that occur in the western United States and that have known N requirements (McCune and Geiser 2009).

Species	N Rating Class[1]	N Requirement	Peak N Deposition Frequency (kg N/ha/yr)
Nephroma laevigatum	O	Low	1.1
Nephroma occultum	M	Mod	2.7
Nephroma parile	M	Mod	2.6
Nephroma resupinatum	O	Low	1.1
Niebla cephalota	O	Low	1.1
Nodobryoria abbreviata	M	Mod	3.1
Nodobryoria oregana	M	Mod	2.6
Parmelia hygrophila	M	Low-Mod	2.5
Parmelia pseudosulcata	O	Low	1.1
Parmelia saxatilis	E	Broad	4.7
Parmelia squarrosa	O	Low	1.1
Parmelia sulcata	E	Broad	6.1
Parmeliopsis ambigua	O	Low-Mod	2.1
Parmeliopsis hyperopta	M	Mod	2.6
Parmotrema arnoldii	O	Low	1.1
Parmotrema chinense	O	Low	1.1
Parmotrema crinitum	O	Low	1.1
Peltigera britannica	O	Low	1.1
Peltigera collina	M	Broad	3.3
Peltigera membranacea	O	Low	1.1
Peltigera neopolydactyla	O	Low	1.1
Physcia adscendens	E	Hi	6.1
Physcia aipolia	E	Hi	6.1
Physcia stellaris	M	Mod	3.0
Physcia tenella	E	Hi	6.1
Physconia americana	M	Mod	3.3
Physconia enteroxantha	E	Hi	6.1
Physconia isidiigera	M	Mod-Hi	3.2

[1] E = eutrophic; M = mesotrophic; O = oligotrophic

Table 12 (continued). List of lichen species that occur in the western United States and that have known N requirements (McCune and Geiser 2009).

Species	N Rating Class[1]	N Requirement	Peak N Deposition Frequency (kg N/ha/yr)
Physconia perisidiosa	E	Hi	6.1
Platismatia glauca	M	Broad	3.1
Platismatia herrei	M	Mod	2.6
Platismatia lacunosa	O	Low	1.1
Platismatia stenophylla	M	Mod	3.7
Polychidium contortum	O	Low	1.1
Pseudocyphellaria anomala	O	Low-Mod	2.3
Pseudocyphellaria anthraspis	O	Low	1.4
Pseudocyphellaria crocata	O	Low	1.1
Pseudocyphellaria rainierensis	M	Mod	2.7
Punctelia subrudecta	E	Hi	6.1
Ramalina dilacerata	E	Mod-Hi	4.8
Ramalina farinacea	E	Broad	5.7
Ramalina menziesii	O	Low	1.1
Ramalina pollinaria	O	Low	1.1
Ramalina roesleri	O	Low	1.1
Ramalina subleptocarpha	E	Hi	6.1
Ramalina thrausta	O	Low	1.1
Sphaerophorus globosus	O	Low	1.1
Sticta fuliginosa	O	Broad	1.1
Sticta limbata	O	Low	1.1
Sticta weigelii	O	Low	1.1
Sulcaria badia	M	Mod	3.4
Usnea cavernosa	M	Mod	3.2
Usnea cornuta	O	Low	1.1
Usnea filipendula	O	Low-Mod	2.1
Usnea glabrescens	M	Mod	3.6
Usnea hirta	O	Low	1.1

[1] E = eutrophic; M = mesotrophic; O = oligotrophic

Table 12 (continued). List of lichen species that occur in the western United States and that have known N requirements (McCune and Geiser 2009).

Species	N Rating Class[1]	N Requirement	Peak N Deposition Frequency (kg N/ha/yr)
Usnea lapponica	M	Mod	3.2
Usnea longissima	O	Low	1.1
Usnea rubicunda	O	Low	1.1
Usnea scabrata	O	Low-Mod	2.3
Usnea schadenbergiana	O	Low	1.1
Usnea subfloridana	E	Hi	6.1
Usnea wirthii	O	Low	1.1
Vulpicida canadensis	O	Low-Mod	2.0
Xanthomendoza fallax	E	Hi	6.1
Xanthoria candelaria	E	Hi	6.1
Xanthoria parietina	E	Hi	6.1
Xanthoria polycarpa	E	Hi	6.1

[1] E = eutrophic; M = mesotrophic; O = oligotrophic

Aquatic Effects

Estuaries and coastal marine waters are generally susceptible to nutrient enrichment effects from atmospheric N deposition because N tends to be the main growth-limiting nutrient in such environments. Growth of plants and algae in fresh waters, in contrast, is often limited by the availability of P, which is typically not an important component of air pollution and atmospheric deposition at most locations. There are some fresh waters, however, that are limited in their algal growth by N or by a combination of both N and P. Many of these occur at high elevation.

High-elevation lakes are of particular concern, among aquatic ecosystems, with respect to potential impacts attributable to atmospheric nutrient N enrichment for several reasons. Many high-elevation lakes tend to be dilute to ultra-dilute and nutrient-poor, contributing to increased risk of biological change from nutrient addition, even in relatively low quantities. Many high-elevation lakes have been shown to be N limited. Diatom communities in several high-elevation lakes in Colorado and Wyoming have been shown to have been impacted by relatively low levels of atmospheric N deposition (Saros et al. 2003, Wolfe et al. 2001). Because soils in the watersheds of high-elevation lakes are often poorly developed, with much exposed bedrock, the transport of N from atmospheric deposition to lake water can be facilitated.

Research by Elser (2009a, 2009b) suggested that atmospheric inputs of N in some high elevation areas have altered the relative availability of N and P to phytoplankton. These changes in nutrient availability may have shifted lakes from N limitation towards P limitation, with consequent

alterations to plankton community structure, species diversity, and trophic interactions (Elser et al. 2009b).

Spatial Patterns in Nutrient Enrichment Risk

Sullivan et al. (2011a) constructed a preliminary overall risk screening assessment to estimate the relative risk to I&M parks and networks of nutrient enrichment impacts from atmospheric N deposition. Similar to the acidification assessment of Sullivan et al. (2011b), this nutrient assessment included consideration of three factors that influence nutrient enrichment risk to park resources from atmospheric N deposition: nutrient N Pollutant Exposure, inherent Ecosystem Sensitivity to nutrient enrichment, and Park Protection mandates. National parks and networks were ranked according to each of these themes. An overall risk ranking was then calculated based on averages of the three theme rankings. This was a coarse screening evaluation, and these rankings are subject to the same limitations as the acidification risk rankings.

Nutrient Nitrogen Pollutant Exposure

Nutrient N Pollutant Exposure was represented by Sullivan et al. (2011b) in multiple variables that reflect N emissions and deposition. Emissions inventories were compiled from the U.S. EPA. However, they are only approximations of actual atmospheric emissions and are less certain for NH_x, as compared with NO_x. Deposition estimates are also uncertain, especially for the dry component of deposition. Estimates of wet plus dry N deposition constructed by Sullivan et al. (2011a) were relatively coarse (12-km grid cells in the East; 36-km grid cells in the West) and could not fully capture spatial variation in deposition that is especially pronounced in areas of complex terrain. Nevertheless, they do provide a reasonable approximation of patterns in N deposition that potentially impact the nutrient status of the ecosystems on which this deposition falls.

Ecosystem Sensitivity to Nutrient Enrichment

The fresh water aquatic and terrestrial ecosystems within the national parks that are thought to be most sensitive to the effects of nutrient enrichment from atmospheric N deposition were assumed to be remote lakes at high elevation, and also alpine, arctic herbaceous, meadow, arid and semi-arid terrestrial vegetation, and wetlands which are transitional between terrestrial and aquatic ecosystems. In general, plant communities that are dominated by herbaceous plants appear to be more sensitive to N enrichment than plant communities dominated by trees. These are the plant community types evaluated by Sullivan et al. (2011a). This does not mean, however, that some of these same effects may not also be occurring in forest or mesic shrub communities.

Nutrient Enrichment Network and Park Rankings

Parks and networks were ranked by Sullivan et al. (2011a) according to perceived risk. The risk rankings were determined by combining the variables that represent nutrient N Pollutant Exposure, inherent Ecosystem Sensitivity to nutrient enrichment, and the extent of existing special Park Protection. Each of these themes was quantified using variables that were available spatially, generally for the entire United States, and that provided insight into the relative differences among parks in these three aspects of overall nutrient enrichment risk.

Networks were ranked for each available emissions or deposition variable, from the network showing the lowest nutrient N Pollutant Exposure (lowest rank) to the network showing the highest nutrient N Pollutant Exposure (highest rank). These variable-specific rankings were then averaged to yield an overall nutrient N Pollutant Exposure ranking for each of the 32 networks, where lower numbers (near 1) reflect lower nutrient N Pollutant Exposure and higher numbers (near 32) reflect higher exposure.

Network designations were calculated in the same manner for the other two nutrient N enrichment themes: Ecosystem Sensitivity to nutrient enrichment and level of Park Protection. Ecosystem Sensitivity was represented by the percent coverage of vegetative types expected to be most sensitive to nutrient N enrichment and the abundance of high-elevation lakes that might be prone to N-limitation. Park Protection was represented by designation as wilderness and/or Class I area. Although these designations do not directly affect risk, they serve to differentiate parks given high levels of protection by law . Finally, an overall risk of nutrient N enrichment effects was calculated as the average of the rankings for the three themes discussed above (Sullivan et al. 2011a).

As for the network rankings, park rankings were calculated individually by Sullivan et al. (2011a) for nutrient N Pollutant Exposure, Ecosystem Sensitivity to nutrient enrichment, and Park Protection metrics. Results of those rankings were summarized by quintile for all parks.

Differences among ranks were most pronounced for the approximately 20% of the networks that showed highest calculated risk. These included four western mountain networks (Sierra Nevada, North Coast and Cascades, Greater Yellowstone, and Klamath), one wetland dominated network (South Florida/Caribbean), one desert network (Mojave Desert), and the Great Lakes Network.

Two of the ranking metrics developed by Sullivan et al. (2011a) are used here to evaluate national patterns in acidification risk among the I&M parks. These are the park-specific nutrient N Pollutant Exposure ranking (Map 17) and the park-specific Ecosystem Sensitivity to nutrient enrichment ranking (Map 18). These two rankings are used to identify the parks, and associated networks, that may have the greatest likelihood of nutrient enrichment damage. Many N-sensitive resources occur in the West, presumably because many of these ecosystems evolved under conditions of low N supply and have low capacity for using additional N.

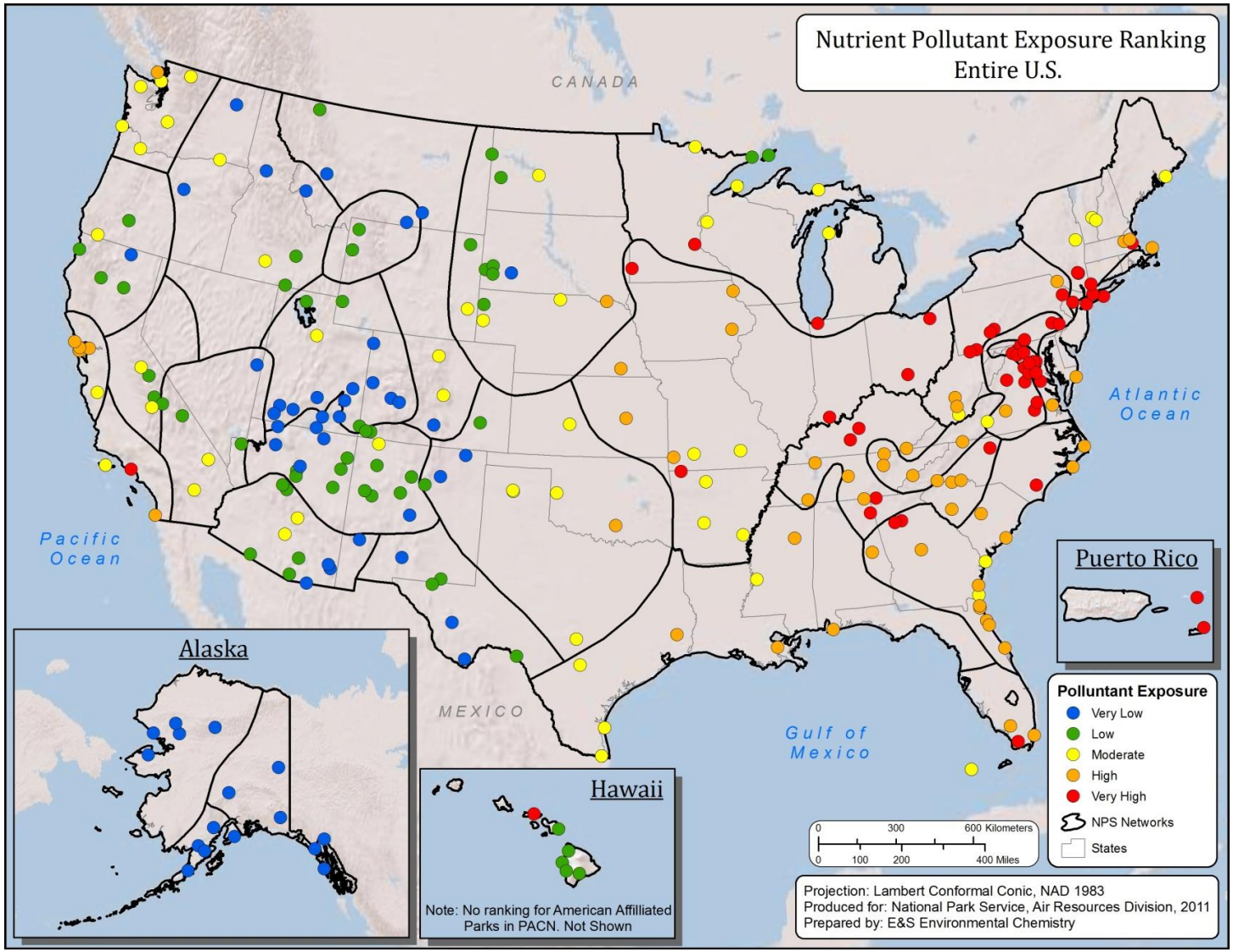
Nitrogen Saturation

An undisturbed, unpolluted forest typically uses and stores, mostly in the soil, almost all of the small amount of N that it receives from atmospheric deposition. This N is cycled between soil and vegetation. However, this cycle can be disrupted by atmospheric N deposition. Forests have a maximum capacity to store N that they receive from outside the watershed. This capacity is determined by the plant species present on the site and the history of logging and other disturbances that removed some of the N previously stored in the soil and trees. When N inputs exceed this storage capacity, the site becomes N saturated, and an appreciable percentage of the incoming N leaches as NO_3^- to soil water and eventually to streams and lakes. This leaching of NO_3^- can contribute to soil acidification, with harmful consequences to plants. During the latter stages of N saturation, tree health deteriorates and the forest may release to drainage water more N than is

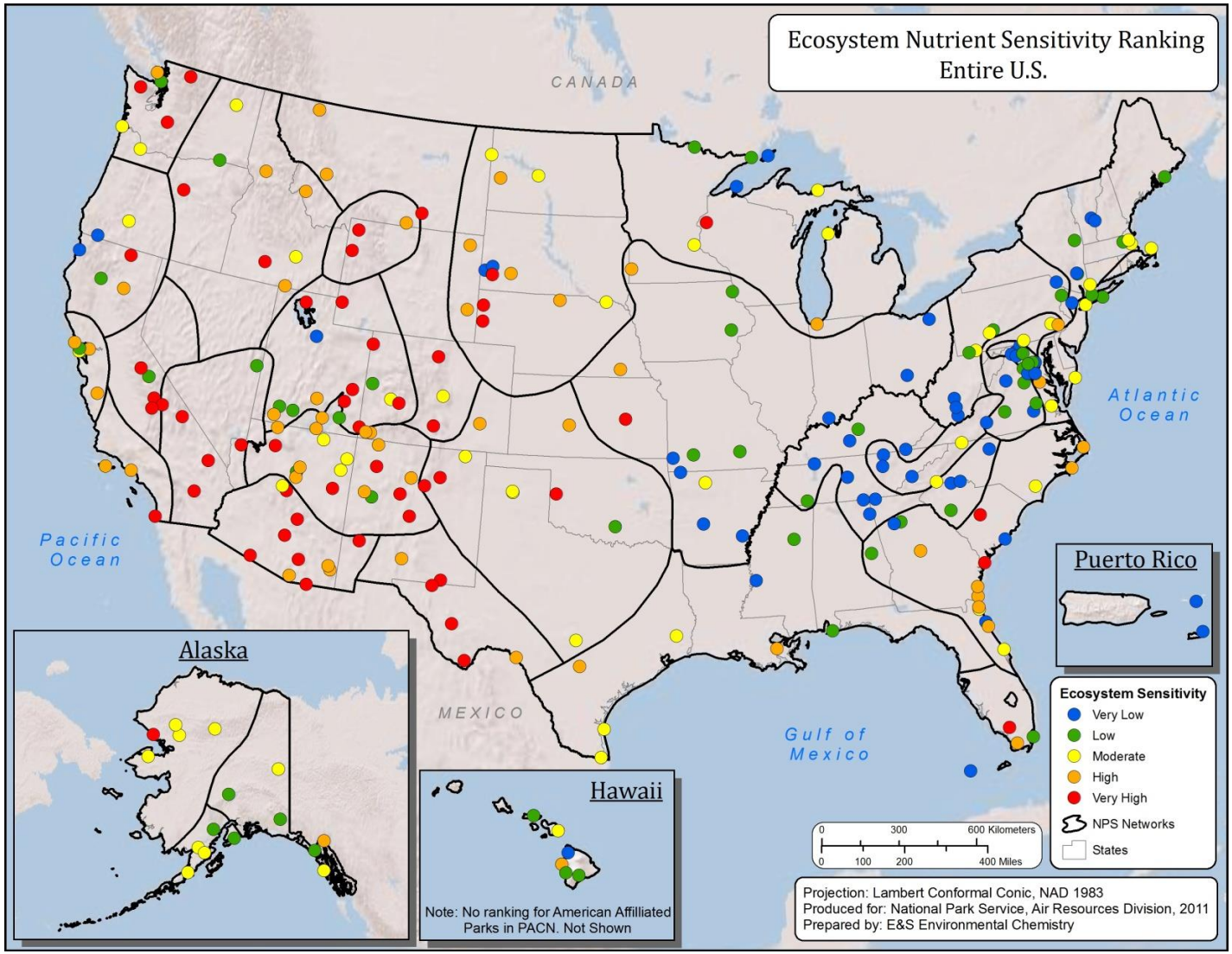
coming into the watershed from atmospheric deposition. Under conditions of advanced N saturation, tree growth declines and sensitive tree species die in response to acidification, Al toxicity, and/or base cation depletion (U.S. EPA 2008).

Some high-elevation spruce forests in the eastern US have become N saturated. In general, hardwood forest stands have not progressed toward N-saturation as rapidly or as far as spruce stands. Hardwood forests may have a greater capacity for N retention than coniferous forests. In addition, hardwood forests are often located at lower elevation and receive lower atmospheric inputs of N (U.S. EPA 2008).

Atmospheric deposition of N has increased N availability in soils at some locations, which has led to increased nitrification and associated acidification of soil and soil water. Because the N retention capacity of soils is strongly dependent on land use history, the relationships between N deposition and ecosystem N status are variable. In general, atmospheric deposition of about 10 kg N/ha/yr or higher is required in order for appreciable amounts of NO_3^- to leach from forest soils to surface waters in the eastern United States and northern Europe (U.S. EPA 2008). At high elevations in the West, the scarcity of soil and dynamics of snowmelt contribute to N leaching at lower levels of atmospheric N deposition (Williams et al. 1996).



Map 17. Park-specific rankings of I&M parks with respect to nutrient N Pollutant Exposure. (Source: Sullivan et al. 2011a)



Map 18. Park-specific rankings of I&M parks with respect to inherent Ecosystem Sensitivity to nutrient enrichment. (Source: Sullivan et al. 2011a)

At some locations, high concentrations of NO_3^- in soil solution appear to be largely responsible for the potentially toxic peaks in Al concentration that sometimes occur in soil solution. Sulfate also plays a role by serving to elevate chronic Al concentrations (Eagar et al. 1996, U.S. EPA 2008).

Many studies in the southern Appalachian Mountains (cf., Joslin et al. 1992, Joslin and Wolfe 1994, Nodvin et al. 1995, Van Miegroet et al. 1992a, 1992b) have found high concentrations of NO_3^- in soil water and stream water at high-elevation spruce-fir forest locations. This NO_3^- leaching is believed to have been caused by high N deposition, low N uptake by forest vegetation, and inherently high N release from soils. Forest age also affects N uptake by vegetation. Mature trees take up relatively small amounts of N for new growth and often show higher NO_3^- leaching than younger, faster growing stands (Goodale and Aber 2001)

Critical Load

The CL is defined as the level, or load, of acid or nutrient pollution below which significant harmful effects are not expected to occur to sensitive ecosystem elements (Nilsson and Grennfelt 1988). Critical loads can be developed for any pollutant, but are most often used for N and S deposition and acidity. Critical loads are commonly expressed as kilograms per hectare (kg/ha) of N or S or as equivalents per hectare (eq/ha) of combined acidity from N and S per unit time (usually per year). The CL is generally calculated for a specified indicator and endpoint for that indicator. For example, a CL for S can be calculated that will prevent ANC from decreasing below 100 µeq/L in a lake, a level considered safe for most aquatic biota. A CL for N can be calculated that will prevent loss of a certain level of plant species diversity in a grassland or alpine meadow. Critical loads can be calculated using dose-response functions, ecological models, or empirical observations. The CL is assumed to be sustainable under long-term steady-state conditions (Henriksen and Posch 2001). In other words, the CL specifies the pollutant load which, when applied to the ecosystem in question for a period of years to centuries, will eventually trigger a change in a chemical or ecological indicator of harm at the time that the ecosystem comes into steady state with respect to that particular pollutant input level.

A dynamic, as opposed to steady-state, pollutant load can also be defined, which is specific to a particular point in time. It will specify, for example, the deposition load that can be tolerated in a certain lake or stream until the year 2100 without loss of brook trout populations. If a stream is already acidified, it can identify how much S or N loading should be reduced in order to restore the stream to a healthy ANC by the year 2100. This dynamic load, which includes consideration of the temporal component of ecosystem damage or recovery, is called a target load (TL). The TL concept can be used to describe not only the effects of time, but also the inclusion of various management perspectives (Sullivan and Jenkins 2014).

There is no single “definitive” CL for a natural resource. The CL depends on what is to be protected, to what level of protection, what indicator is used, and what is specified as the critical or threshold tipping point level. Critical load estimates reflect the current state-of-knowledge and policy priorities, both of which can change over time. Changes in scientific understanding may include development of new dose-response relationships, better resource maps and inventories, larger survey datasets, more data from monitoring, and improved numerical models. Changes in the policy elements may

include new mandates for resource protection, focus on new pollutants, and inclusion of perceived new threats such as climate change or invasive species that may exacerbate the pollutant effects under consideration (U.S. EPA 2008). This process typically results in calculation of multiple CLs for a given pollutant at a given location, and those values can change over time. Multiple CL values may also arise from an inability to agree on a single definition of significant harm (Sullivan and Jenkins 2014).

The CL is affected by the heterogeneity of natural ecosystems. Because of high spatial and temporal variability of soils and surface waters, there may be a continuum of CL values for a given sensitive indicator. Multiple values (or a range of values) will result from the CL analysis in most cases.

The CL or TL provides an indication of the point at which the ecosystem may begin losing ecosystem services (ES) and transitioning from a sustainable functioning ecosystem to one that is not functioning properly and is no longer considered sustainable. The CL concept provides a tool that enables the implementation of ES-based decision making (Sullivan 2012).

On its own, the CL does not predict whether the ecosystem under investigation actually experiences, or will in the future experience, any biological harm. To make that determination, the ambient pollutant load must also be considered. If the ambient deposition is higher than the CL or TL that the ecosystem can tolerate, the ecosystem is said to be in exceedance. Transitioning between a condition of non-exceedance to a condition of exceedance does not mean that the ecosystem is currently experiencing damage. The transition from non-exceedance to exceedance, or vice versa, indicates a change in the probability that ES will be lost or recovered, depending on whether the starting point is an undamaged or a damaged state (Sullivan 2012). For undamaged systems, exceedance signifies that if deposition is continued at the current exceedance level, damage will occur at the time point specified for the analysis (e.g., 2100, steady state condition). Transitioning from exceedance to non-exceedance suggests that recovery will occur at the future time specified in the analysis.

In a watershed that receives a loading of acidic deposition that is lower than the CL, a TL might be selected for policy purposes that is higher than or lower than the CL. A higher TL might be justified if the damage projected to occur under the CL will not be manifested for a very long time, allowing future opportunity to further mitigate pollution levels before the damage is realized. A lower TL might be justified in an effort to err on the side of resource protection or to protect against short-term damage prior to attaining a long-term steady-state protected condition. For a watershed that currently receives an acidic deposition loading that is higher than the CL (damaged resource or projected to become damaged), an interim TL might be selected that is higher than the CL in order to allow for partial resource recovery within a management timeline. Alternatively, for an already damaged watershed, a TL might be selected that is lower than the CL if resource managers are unwilling to wait the decades or centuries that it might take to achieve full resource recovery under sustained loading at the CL level (Sullivan 2012).

Pardo et al. (2011) compiled empirical data on nutrient-N CLs in ecoregions throughout the United States for a variety of N-sensitive resources, including lichens, mycorrhizal fungi, herbaceous plants and shrubs, and forests. These CLs were generally reported by Pardo et al. (2011) as ranges for a

given ecoregion. Because ecosystems vary, sometimes substantially, within an ecoregion, the CL range for a given receptor may not apply to all plant communities or all portions of the ecoregion. When selecting appropriate CL for a specific national park it is important to examine the scientific basis of the CL, that is, whether the CL estimate was based on a specific vegetation type, and whether that vegetation type occurs in the park. Pardo reported CL values as "reliable," "fairly reliable," and "expert judgment." Table 13 lists their suggested CL levels considered "reliable" on the basis of comparable findings from multiple studies. Although Table 13 lists only CL values rated as "reliable," CLs rated as "fairly reliable" and "expert judgment" might also be useful in identifying areas and resources that are potentially at high risk from N deposition. Reported CL values were highly variable for different ecoregions and ecosystem components. Current deposition exceeded critical loads for a number of ecoregions and indicators, suggesting that these ecoregions and indicators were at risk of harm from N deposition.

Sullivan and McDonnell (2014) evaluated empirical CL estimates for ecoregions developed by Pardo et al. (2011) and analyzed available vegetation data to estimate the appropriate CL range for 12 selected national parks in the intermountain West. They also examined N oxide emissions by county and total (oxidized and reduced) N deposition estimates in and near the selected parks. Deposition estimates for 2008 were compared to park nutrient-N empirical CL to evaluate the likelihood that CL were exceeded in NPS areas. The parks selected for study included many of those that have been identified as having N-sensitive ecosystems. Some of the parks have been experiencing in recent years increasing levels of nearby energy, agricultural, mineral extraction, and/or transportation development, with associated increasing N emissions.

The CL and exceedance estimates presented by Sullivan and McDonnell (2014) were based on the lower limits of the ranges of CL, by ecoregion, reported by Pardo et al. (2011). This was done to conform with the NPS mandate when considering CL to err on the side of resource protection. Based on these lower limits of the CL ranges reported by Pardo et al. (2011), terrestrial resources in most of the parks evaluated by Sullivan and McDonnell (2014) were either in exceedance of the nutrient-N CL or received ambient (year 2008) total wet plus dry N deposition that was below, but within 1 or 2 kg N/ha/yr of, the CL. Thus, nutrient sensitive terrestrial resources in some of these parks may be experiencing adverse impacts associated with CL exceedance. In other cases, appreciable increases in NO_x or ammonia (NH_3) emissions and deposition may trigger exceedances in the future.

Of the 12 parks that were evaluated in the study of Sullivan and McDonnell (2014), estimated nutrient-N CL exceedances were most pronounced in Voyageurs (VOYA), Mesa Verde (MEVE), Black Canyon of the Gunnison (BLCA), and Saguaro (SAGU) national parks. Large portions of Grand Canyon (GRCA), Arches (ARCH), Badlands (BADL), Theodore Roosevelt (THRO), and Wind Cave (WICA) national parks and Colorado (COLM) and Dinosaur (DINO) national monuments received N deposition in 2008 that was within 1 kg N/ha/yr or less below the nutrient-N CL. Much of Canyonlands National Park (CANY) received N deposition in 2008 that was below, but within 2 kg N/ha/yr of, the nutrient-N CL. These results provide estimates of relative risk of nutrient enrichment to sensitive vegetative receptors among the parks selected for study.

Table 13. Selected empirical critical loads of nutrient nitrogen for U.S. ecoregions. All critical loads listed here were judged as reliable (adapted from Pardo et al. 2011).

Ecoregion	Ecosystem Component	Critical Load for N Deposition (kg/ha/yr)	Response
Tundra	Prostrate dwarf shrubs	1-3	Changes in CO_2 exchange, cover, foliar N, and community composition of vascular plants
Taiga	Shrublands	6	Shrub cover decreased, grass cover increased, increased parasitism of shrubs
Northern Forests	Hardwood and coniferous forests	8	Increased surface water NO_3^- leaching
Northwestern Forested Mountains	Alpine lakes	1.5	Diatom assemblages – change in diversity
Northwestern Forested Mountains	Lichens	2.5-7.1	Epiphytic lichen community change, thallus N enrichment in mixed-conifer forests (non-Alaska)
Northwestern Forested Mountains	Subalpine forest	4	Increase in organic horizon N, foliar N, potential net N mineralization, and soil solution N, initial increases in N leaching below the organic layer
Northwestern Forested Mountains	Alpine grassland	4-10	Changes in plant species composition
Northwestern Forested Mountains	Mixed conifer forest	17	NO_3^- leaching
Marine West Coast Forests	Western OR and WA forests	2.7-9.2	Epiphytic lichen community change
Eastern Temperate Forests	Eastern hardwood forests	8	Increased surface water loading of NO_3^-
Mediterranean California	Mixed conifer forests; lichens	3.1-5.2	Lichen chemistry and community changes
Mediterranean California	Serpentine grassland	6	Annual grass invasion, replacing native herbs
Wetlands	Intertidal wetlands	50-100	Loss of eelgrass
Freshwaters	Western Lakes	2	Freshwater eutrophication

The emissions and deposition data provided in that report were estimates for 2008 and may not fully capture current emissions and deposition levels, particularly in areas where NO_x and/or NH_3 emissions have recently increased. Thus, it will be important to continue to track N emissions and

deposition and to evaluate likely impacts on CL exceedance and associated impacts on nutrient-sensitive vegetation in these, and perhaps other, national park units.

Baron (2006) recommended a critical load of 1.5 kg N/ha/yr (wet deposition) to protect alpine lakes in ROMO against eutrophication. Similarly, Saros et al. (2011) found that 1.4 kg N/ha/yr (wet deposition) caused nutrient enrichment effects (i.e., changes in diatom diversity) in high elevation lakes in the eastern Sierra Nevada and the Greater Yellowstone ecosystems.

Nitrogen deposition to wetlands can alter competitive relationships among species, sometimes increasing the establishment of non-native species at the expense of rare species. Such changes are thought to occur in Europe at N deposition levels in the range of 5 to 10 kg N/ha/yr for raised and blanket bogs, 10 to 20 kg N/ha/yr for poor fens, and at higher deposition levels for rich fens and salt marshes (Achermann and Bobbink 2003). Some wetland plants appear to be adapted to low-N environments. These include some species in the genera *Sphagnum* and *Isoetes* and some insectivorous plants, such as the green pitcher (*Sarracenia oreophila*) and the roundleaf sundew (*Drosera rotundifolia*). The pitcher plant *Sarracenia purpurea*, which is native to nutrient-poor peatlands in the eastern United States, has been proposed as an indicator of atmospheric N supply (Ellison and Gotelli 2002). Modeling results suggest that N deposition increases the extinction risk of pitcher plant populations (Gotelli and Ellison 2002, 2006). Pardo et al. (2011) suggested a critical load range of 2.7-13 kg N/ha/yr to protect wetlands in the northeastern U.S., and a range of 6.8-14 kg N/ha/yr to protect pitcher plant populations.

Ozone Exposure

Ozone Production and Dispersion

Ozone is an important atmospheric pollutant throughout substantial portions of the United States, with relatively high levels in urban areas and at many remote locations, including within some national parks. Ozone is not emitted directly into the atmosphere by pollutant sources. Rather, it is produced in the atmosphere by photochemical reactions that involve atmospheric NO_x and VOC precursors. These reactions are driven by ultraviolet radiation from the sun. The O_3 precursors are emitted by motor vehicles, power plants, and industry in the case of NO_x, and by industries that use organic chemicals and by natural vegetation in the case of VOCs. Ozone builds up to relatively high levels primarily during summer when abundant sunlight powers the photochemical reactions that produce O_3 (Kohut 2007a).

Ozone is a colorless gas and is a component of smog, which can develop during the clear warm weather associated with high pressure systems and low wind speeds. It is an important regional pollutant of interest in national parks because it forms during atmospheric transport of its precursors and can occur at high concentrations in areas remote from precursor sources. Dispersion and transport of pollutants vary locally.

The challenge is to quantify the spatial distribution of O_3 exposure relative to the location of sensitive plant receptors and the environmental conditions that promote O_3 uptake by plants. The fact that O_3 concentrations are higher downwind from urban areas, and that concentrations tend to increase with elevation, suggests that some national park lands can be particularly vulnerable.

Despite known general relationships between regional "sources" of O_3 (and its precursors) and wildland "receptors", it has been difficult to estimate O_3 exposure in those wildlands because of high variability. Ozone is monitored at about 40 national parks, although about twice that many urban national park units have nearby O_3 monitors. NPS ARD also provides estimates of O_3 concentrations and exposures at over 200 park units in the continental U.S., using all available monitoring data to derive interpolated estimates (http://www.nature.nps.gov/air/Maps/AirAtlas/index.cfm)

Forest fires emit considerable quantities of NO_x and hydrocarbons, and therefore can contribute to O_3 formation. The concentration of O_3 in the atmosphere in the nonurban western United States has increased since the late 1980s by about 5 parts per billion by volume (ppbv; Jaffe and Ray 2007). Jaffe et al. (2008) investigated the role of forest fire in this trend. The summer burned area was significantly correlated with O_3 concentration at CASTNET and NPS atmospheric chemistry monitoring sites. For mean and maximum fire years, the concentration of O_3 in the atmosphere was increased by fire by an average of 3.5 and 8.8 ppbv, respectively. The estimated amount of biomass consumed was a slightly better predictor of O_3 concentration than burned area. This relationship between atmospheric O_3 concentration and burned area or biomass consumed is especially important because the frequency of extreme fire years in the western United States appears to be increasing (Jaffe et al. 2004) due to increased spring and summer temperature, earlier snowmelt, and dryer forest conditions (Cook et al. 2004, Westerling et al. 2006).

Jaffe et al. (2008) concluded that the increase in fires in the western United States has largely been responsible for the observed increase in summer O_3 concentrations reported by Jaffe and Ray (2007). Increasing temperature in the future will likely further influence the effects of fire on O_3 formation.

Understanding the contribution of N oxides to O_3 formation during transport from pollutant source region to national parks and the effects of local photochemistry on O_3 formation are also important in developing predictions of O_3 exposure. Planned future reductions in NO_x emissions from upwind point and mobile NO_x sources will contribute to decreased O_3 exposure in many areas (Tong et al. 2005).

Ozone is a particular threat to relatively high-elevation plant species because concentrations and total exposure can be higher at high elevations under appropriate atmospheric conditions (Brace and Peterson 1996, 1998, Loibl et al. 1994, Sandroni et al. 1994). Exchange of O_3 between the stratosphere and troposphere can contribute to the natural background O_3 concentration at both high- and low-elevation locations (Lefohn et al. 2011).

The background O_3 concentration is not known with a high degree of certainty, partly because of different ways of defining it and partly because it is not a measurable condition. The level of O_3 in a "pristine" area may have a weekly average as low as 10 to 25 ppbv (Altshuller and Lefohn 1996, Cooper and Peterson 2000), with maximum hourly O_3 concentrations generally less than about 50 to 80 ppbv. Human activities influence O_3 concentration throughout the Northern Hemisphere. Changes not normally associated with air pollution, such as widespread agriculture and landscape vegetation changes, have also changed the background O_3 level. EPA (2006) defined a policy-relevant background O_3 concentration as the amount of O_3 that would be present in the atmosphere under a

scenario of zero North American anthropogenic precursor pollutant emissions. EPA estimated the policy-relevant background in the range of 20 to 40 ppbv of O_3 (Fiore et al. 2003), of which half or more is estimated to be of anthropogenic origin outside North America (Lamarque et al. 2005, Mickley et al. 2001, Shindell and Faluvegi 2002). In the more recent Policy Assessment for the O_3 National Ambient Air Quality Standards (NAAQS; U.S. EPA), EPA estimated that natural background levels range from approximately 15-35 parts per billion (ppb; median value of 24 ppb), with the highest values at high elevation sites in the western United States. Natural background levels are higher at these high-elevation locations primarily because natural stratospheric O_3 impacts and international transport impacts increase with altitude (where O_3 lifetimes are longer).

Much of that anthropogenic component of the policy-relevant background originates from Asia. Emissions of NO_x in Asia have increased dramatically in recent years, and may account for about 3 to 7 ppbv of O_3 in parts of the United States (Zhang et al. 2008).

Nonattainment of O_3 standards in the southeastern United States, where O_3 concentrations tend to be relatively high, has been attributed to oxidation of atmospheric NO_x in the presence of large amounts of VOC, much of which is biogenic isoprene (Chameides et al. 1988). Within southeastern rural areas, biogenic VOCs emitted by vegetation (Fuentes et al. 2000) and non-biogenic VOCs emitted by human activities are both common in the atmosphere (Hagerman et al. 1997, Kang et al. 2001). It is important to understand the role of these VOCs in O_3 formation in order to devise effective control strategies for O_3 (Kang et al. 2003). Rural areas in the Southeast are generally considered to be NO_x-limited for O_3 formation (Hagerman et al. 1997); nevertheless, local VOC emissions can also be important (Kang et al. 2003).

Ground-level O_3 is a particular concern for national park lands because remote areas can experience greater cumulative O_3 exposure and higher minimum and maximum concentrations than the upwind urban and industrial areas where most of the pollutant precursor sources are located (Brace and Peterson 1998). In many places, O_3 concentrations tend to increase with elevation (Brace and Peterson 1998, Cooper and Peterson 2000), although there are some exceptions (Bytnerowicz et al. 1999). This can lead to elevated values in mountainous locations (Aneja et al. 1991), some of which occur in national parks.

The occurrence of peak O_3 concentrations higher than 100 ppb during the growing season is generally on the decline throughout the United States (Smith 2012). Moderate O_3 concentrations are becoming more widespread in rural areas (Percy et al. 2003). In response to the observed declines in peak exposures, the occurrence of foliar symptoms has also declined in eastern forests, especially since 2002 (Smith 2012). However, quite high O_3 concentrations have been observed in locations downwind of O&G development in Wyoming, Utah, and Colorado in recent years. For example, one-hour concentrations as high as 149 ppb, and many days with 8-hour O_3 exceedances of the NAAQS were recorded in the Uintah Basin of Utah in 2010 (Lyman and Shorthill 2013). The O_3 NAAQS is currently set at 75 ppb, based on the annual fourth-highest daily maximum 8-hr concentration, averaged over 3 years.

Effects of Ozone on Plants

Ozone injury to plants is determined primarily by three things: 1) the plant and its inherent sensitivity to O_3, 2) the level of O_3 in the atmosphere at the location of the plant, and 3) site-specific environmental conditions. In general terms, O_3 injury will only occur if the plant is genetically predisposed to O_3 injury, the level of atmospheric O_3 exposure exceeds the threshold for injuring that plant, and the environmental conditions at the site facilitate the uptake of O_3 into plant leaves. This triad concept of O_3 injury was described by Kohut (2007a).

Under the triad concept, injury occurs when all three key elements are satisfied. First, the plant must be predisposed to O_3 sensitivity. Differences in sensitivity are often pronounced at the species level. For example, ponderosa pine (*Pinus ponderosa*) and quaking aspen (*Populus tremuloides*) are two common tree species found in many national parks in the western United States that are known to be highly sensitive to O_3. However, differences in plant sensitivity can also be observed among clonal lines, subspecies, or individual plants. The reasons for such differences are not well understood (Kohut 2007a). Second, the threshold level of atmospheric O_3 exposure that can produce injury on a plant must be exceeded at the location of the plant. Very high levels of exposure can produce acute effects; lower but sustained levels of exposure can produce chronic effects. Exposure indices that consider both atmospheric O_3 level and duration of exposure are used to evaluate the likelihood of the plant experiencing a high O_3 dose. Third, the plant must experience a range of environmental conditions that facilitate O_3 uptake into the leaf through the stomata. The environmental conditions that inhibit stomatal opening, and therefore also inhibit O_3 uptake into the leaf, include mainly low soil moisture and high temperature. Conditions of optimum moisture availability, humidity, illumination, and temperature facilitate both photosynthesis and uptake of O_3 into the leaf. Such conditions can be highly variable spatially. For example, low soil moisture and high temperature can limit stomatal opening broadly across a vegetative community, yet more favorable conditions for O_3 uptake may occur at the microsite level, for example in riparian zones or other areas that retain soil moisture. Thus, plants on favorable microsites may exhibit foliar O_3 symptoms, whereas adjacent plants may not. Similarly, an ecosystem may experience O_3 symptoms during one year, but not the next, due entirely to differences in soil moisture and temperature. Foliar symptoms are most pronounced when all variables of the response triad are satisfied: that is, when a sensitive plant species or genotype is exposed to atmospheric O_3 levels above the injury threshold under environmental conditions that foster O_3 uptake into foliage (Kohut 2007a).

Visible foliar symptoms provide an easily identified indicator of O_3 effects on vegetation. Ozone injury of cells and tissues is essentially the same in woody and herbaceous plants (Bytnerowicz and Grulke 1992). Injury generally occurs first in the most photosynthetically active tissues, with disruption of chloroplasts in the palisade and mesophyll tissue. The loss of photosynthetic tissue results in visible chlorosis and necrosis. Visible symptoms do not constitute an early warning signal indicating damage to the plant; physiological impacts may have occurred prior to the production of foliar symptoms. Various effects may have occurred inside the plant before visible symptoms are evident. Furthermore, the presence of visible symptoms does not necessarily indicate that effects on growth, health, or reproduction have, or will, also occur.

Standards and Cumulative Exposure Indices

Evaluation of plant response to O_3 exposure requires use of an appropriate O_3 exposure or dose summary statistic. Exposure reflects the atmospheric concentration of O_3 to which a plant is exposed; dose reflects the amount of O_3 that is actually taken up by the plant. Factors that influence plant response are complex and vary with environmental conditions and the physiology of O_3-sensitive plants (Musselman et al. 2006). The degree of pollutant injury depends on the effective dose, which is a function of concentration, length of exposure, and stomatal aperture, as well as plant biochemical defense response to the O_3 dose (Kozlowski and Constantinidou 1986). Exposure indices are unable to consider the full range of processes that control O_3 transport from the atmosphere into the leaf or the physiological response, including detoxification mechanisms, of the plant. As a consequence, there is no appropriate dose-based index for use in evaluating the effects of O_3 on plants (Musselman et al. 2006). Rather, exposure-based indices are used.

In order to protect human health and welfare, EPA has established primary and secondary NAAQS for maximum allowable atmospheric O_3 concentration levels. Prior to 1997, these standards were based upon 1-hour average O_3 measurements. They were revised in 1997, when the EPA promulgated new standards, both primary and secondary, based upon an 8-hour average value. The standards were set at 0.08 ppm (parts per million; or rounded to 85 parts per billion - ppb), a value that represented the annual fourth-highest daily maximum 8-hour O_3 concentration, averaged over three years for the protection of both human health (primary NAAQS) and vegetation (secondary NAAQS). The standards were strengthened in 2008 to 0.075 ppm. This average is computed by first determining the highest 8-hour average O_3 value for each day of the year at a site, and then identifying the 4^{th}-highest of all daily maximum 8-hour O_3 values that occurred during the year. These 4^{th}-highest values are then averaged over three successive years to determine the final concentration value that is compared to the standard.

The decision by the U.S. EPA to transition from an O_3 standard based upon a 1-hour average to a standard based upon an 8-hour average was prompted by research indicating that prolonged exposure to O_3 at concentrations lower than the 1-hour standard can have significant impacts. The EPA has also recognized the potential importance of an exposure index in setting the secondary O_3 standard to protect native vegetation and ecosystems. The U.S. EPA proposed a new secondary O_3 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, called the W126, of the total plant O_3 exposure during the daytime (8:00 AM – 8:00 PM), whereby hourly values were weighted according to magnitude and then summed. Higher concentrations are weighted more heavily, as they are more likely to induce O_3 injury.

The W126-3 month statistic is calculated as the three-month period having the highest cumulative exposure. The proposed standard was based on a three-year average of the annual W126-3 month metric. EPA proposed to set the level of the new secondary standard in the range of 7-15 ppm-hr. EPA also proposed a stronger primary standard, in the range of 60-70 ppb. The NPS supported the stronger standards, recommending a secondary standard in the range of 7-9 ppm-hours (U.S. DOI-

NPS 2010). After a period of review, the EPA decided in 2011 to defer setting standards at that time, retaining the previous standards of 75 ppb.

In addition to the W126, another metric, the SUM06, is used to express O_3 exposures (Heck and Cowling 1997). This index is calculated as a 90-day maximum sum of the hourly concentrations of O_3 during daylight hours that are higher than or equal to 60 ppb (0.06 ppm). It is calculated over a running 90-day period. The maximum value can occur at any time of year during the O_3 monitoring season, but usually occurs during the summer months.

The W126 index (Lefohn et al. 1997) can be calculated as the weighted sum of the 24 1-hour O_3 concentrations measured daily from April through October (7 months) as originally proposed by Lefohn or calculated for daylight hours over a 3-month period as modified by the U.S. EPA. When originally developed, the W126 was expressed in conjunction with the number of hours (called the N100) during which the O_3 exposure is $\geq$ 100 ppb. In its proposal for a secondary standard, EPA recommended using the 3-month W126 without the N100. They noted that there was little research on the N100, and the W126 already preferentially weights higher O_3 concentrations, giving all concentrations over 100 ppb the highest weighting value.

It is important to note that calculated values of the W126 index differ depending on whether they are calculated over a seven-month period (W126-7mo; original Lefohn version) or a three-month period (W126-3 mo; modified by EPA in 2010). The O_3 assessments of Kohut (2007a, b) used the Lefohn version; the assessment presented here uses the EPA version. NPS has adopted the EPA version for assessing O_3 exposure in parks with respect to potential injury to vegetation (NPS 2011).

In December, 2014, EPA proposed revising the O_3 standard to a value in the range of 65-70 ppm based on an 8-hr average. A value in this range would be equivalent to a range of W126 values below 13-17 ppm-hrs (3 month), well above the NPS recommendation of 7-9 ppm-hrs.

Manifestation of Plant Injury

In the context of impacts of air pollutants on plants, damage and injury terminology is rather precise, as applied by FLMs (cf., Guderian 1977, Musselman et al. 2006, U.S. Forest Service et al. 2010). Injury refers to all physical and biological responses to air pollutants, including effects on processes and cycles. Damage is a reduction in the intended use or value of the resource, including reduction in ecosystem services, aesthetic value, or plant diversity.

Ozone can cause injury to various plant tissues, including direct effects on leaves and indirect effects on stems and roots. Manifestation of foliar symptoms is the most visible indication of increased O_3 injury, although O_3 symptoms can sometimes be confused (without proper field training) with other biophysical injuries, including abrasion, desiccation, insect herbivory, and effects of fungal pathogens. Common indicators of O_3-induced foliar symptoms are summarized in Table 14. It is difficult to correlate visible O_3-induced foliar symptoms with other effects on vegetation, such as on growth or reproduction. The significance of foliar symptoms appears to depend on how much of the total leaf area is affected and also plant age, size, and developmental stage.

Table 14. Common symptoms of O3-induced foliar injury (from Krupa and Manning 1988, Krupa et al. 1998, Sullivan et al. 2001)

Plant Type	Acute Symptoms	Chronic Symptoms
Conifers	• Banding; clear bands of chlorotic tissue develop on semi-mature needle tissue following O_3 episodes. • Tipburn; characterized by dying tips of young elongating needles. At first reddish-brown in color later turning brown, injury spreading	• Flecking[1] and mottling[2] ; flecking is the earliest symptom on the older needles of conifers. Mottling is generally associated with diffuse chlorotic areas interspersed with green tissue on first-year needles. • Premature senescence; early loss of needles.
B Broad-leaved plants (hardwood trees, herbaceous plants)	• Bleaching (unifacial or bifacial); small unpigmented necrotic spots or more general upper surface bleaching. Palisade cells and, where injury is more severe, upper epidermal cells collapse and become bleached. • Flecking; small necrotic areas due to death of palisade cells, metallic or brown, fading to tan, gray or white. • Stippling; small pigmented spots where a few palisade cells are dead or injured, may be white, black, red, or red-purple. • Bifacial necrosis; when the entire tissue through the leaf is killed, bifacial dead areas develop, ranging in color from white to black. While small veins are usually killed along with the other tissue, larger veins frequently survive	• Pigmentation (bronzing); leaves turn red-brown to brown as phenolic pigments accumulate. • Chlorosis. • Premature senescence; early loss of leaves, flowers, or fruit.

[1] Flecking is necrosis of tissue in small areas that may coalesce.

[2] Mottling is variation in chlorosis over the leaf surface, without necrosis.

Nevertheless, visible foliar symptoms have been shown in some studies to correlate with decreased plant growth (cf., Benoit et al. 1982, Karnosky et al. 1996, Peterson et al. 1987) and, in some cases, decreased reproduction (cf., Black et al. 2000, Chappelka 2002). Ozone enters plant leaves as a gas and dissolves in the presence of water. The resulting free radicals oxidize proteins of cell membranes, including those of the thylakoid membranes where photosynthesis takes place. Injury includes leaf discoloration, reduced photosynthetic rates, lowered sugar production, reduced growth, and possibly plant death.

Ozone exposure is believed to inhibit plant stomatal responses. This may explain the finding of McLaughlin et al. (2007a, 2007b) that peak hourly O_3 exposure increased water loss from several tree species and reduced late-season modeled stream flow in forested watersheds in eastern Tennessee. Ozone exposure was also found to decrease net primary productivity (NPP) of most forest types in the mid-Atlantic region by 7 to 8%, but had a much smaller effect (~ 1%) on the NPP of high-elevation spruce-fir forests (Pan et al. 2009).

The timing of O_3 exposure relative to the life cycle of the affected plant is important in determining response. For instance, exposure to O_3 may reduce the growth of the root system in an annual plant; as the plant repairs leaf injury and maintains photosynthesis there is less C available to grow roots (U.S. EPA 1996b). In fact, root systems may be reduced in growth long before deleterious effects are manifested on above-ground portions of the plant. In perennial plants, the process is complex, as stored reserves are usually available for growth and the effect of an exposure may not be manifested for several growing seasons (Andersen et al. 1991, Hogsett et al. 1989, Laurence et al. 1994). However, in the most sensitive perennial species, a single season of exposure can be sufficient to reduce growth significantly (Wang et al. 1986, Woodbury et al. 1994). The EPA estimated that under ambient O_3 exposures, biomass loss in quaking aspen could exceed 10% in some areas of the East; biomass loss in black cherry (*Prunus serotina*) seedlings could exceed 20% in many areas (U.S. EPA 2007). Impacts to seedlings may decrease long-term growth and survival, ultimately affecting both individuals and populations of sensitive species.

Ozone enters the plant through stomata, so the duration of stomatal opening greatly affects the pollutant dose assimilated. Once O_3 enters a plant cell, there are many biochemical processes that can be affected (Heath and Taylor 1997, Wellburn 1988). Ozone increases the potential for the formation of free radicals, which are highly reactive and disrupt various metabolic processes through oxidation, substitution for other compounds, and toxicity. Disruption of photosynthetic processes results in lower photosynthetic rates (Grulke 1999, Patterson and Rundel 1989), reduces plant vigor and productivity, and can affect internal resource allocation (Matyssek and Innes 1999).

The most common visible effects on vegetation of O_3 exposure are stipple (pigmentation on leaves), fleck (tiny light colored markings on upper layers of leaves), mottle (blotchy appearance), and necrosis (death of tissue; Brace et al. 1999, Hogsett et al. 1989, Miller et al. 1983, Stolte 1996, Thompson et al. 1984a, Thompson et al. 1984b, Treshow and Anderson 1989). Oxidant stipple is highly specific to O_3 injury. Other types of injury may also occur in response to O_3 exposure, including chlorosis, premature senescence, and growth reduction. However, these types of injury are not specific to O_3 and can be caused by a variety of stressors. Documentation of stipple provides a

strong indication of O_3 injury; changes in growth, species composition, and diversity in response to O_3 exposure are much more difficult to document and quantify in the field.

Visible symptoms on leaves usually occur after acute exposure to high concentrations of O_3. Exposure to moderate concentrations of O_3 for several days to several months can also cause chronic injury, accelerated aging, premature casting of foliage, or reduced growth (Pell et al. 1994a, Pell et al. 1994b, U.S. EPA 1996a, U.S. EPA 1996b). Accelerated aging may result in premature color change and loss of foliage, an effect of considerable importance at some national parks where park visitation levels are relatively high during the fall color season. Growth reductions at ambient levels of O_3 are often difficult to measure, although a cumulative stress over multiple growing seasons may significantly reduce the growth and productivity of trees and understory vegetation (Reich and Amundson 1985, U.S. EPA 1996b).

Ozone exposure typically does not kill the plants outright. Rather, it weakens them by disrupting their C budget. Exposure to O_3 contributes to reduced C fixation. In addition, because C is needed to repair O_3 injury to membranes and organelles, there is less C available in O_3 stressed plants for growth, reproduction, or responding to other stressors such as low temperature, insects, and disease. Plants must expend energy to counteract the effects of O_3. This energy might otherwise be used for growth or health maintenance. Injured plant cells may die if detoxification and cellular repair are outpaced by O_3 uptake into plant tissue.

There is considerable genetic variability, both within and among plant species, in plant response to O_3 exposure (Miller et al. 1982). The most sensitive plants are injured by exposure to concentrations of 60 ppbv or less for several days and can often be used as biological indicators of O_3 exposure (U.S. EPA 1996b). Conversely, some plants are very tolerant of O_3 and are unaffected, even in severe exposures. Stomatal responses to O_3 exposure are very complex. There can be pronounced differences in stomatal response due to differences in species sensitivities, exposure levels, and duration of exposure (McAinish et al. 2002, McLaughlin et al. 2007a).

Oxidant stipple can occur on sensitive plant species at O_3 concentrations considered to be near or at background levels (Singh et al. 1978), sometimes in response to naturally occurring stratospheric O_3 intrusions. However, such intrusions typically occur during spring, and not during the major part of the growing season (Lefohn 2011, Singh et al. 1980, Wooldridge et al. 1997).

Field Observations

Smith (2012) reported results of O_3 exposure and effects biomonitoring across the northeastern and north-central United States, with data collected over a period of 16 years at some locations (biosites). Ozone-sensitive plants were evaluated for O_3-induced foliar symptoms. However, regression models were generally not successful in predicting the presence of foliar symptoms based on O_3 exposure (SUM06 and N100), site moisture (Palmer Drought Severity Index [PDSI]), and a plant moisture availability index [MI]; $R^2 \leq 0.1$). She did generate plausible clustering of the data that supported the following weak associations:

- biosites showing no symptoms occurred across all SUM06 and N100 exposures;

- biosites showing symptoms occurred across all SUM06 and N100 exposures;
- when PDSI and MI indicated that moisture was limiting, the percent of sites not showing symptoms was much greater than the percentage showing symptoms.

Generally similar results were reported by Campbell et al. (2007) for western forests. They found a general association between foliar symptoms and exposure, but high symptom expression could occur with low O_3 exposure, and vice versa.

Field studies and controlled exposure experiments continue to identify O_3-sensitive plant species (cf., Kline et al. 2008, Kline et al. 2009). The U.S. Forest Service's Forest Inventory Analysis (FIA) Program routinely surveys the incidence and severity of O_3-induced foliar symptoms on multiple sensitive species using standardized procedures at biosites throughout the United States (Coulston et al. 2003, Smith et al. 2003, USDA FS 2011). These monitoring data have confirmed the applicability of several species as effective biomonitors in the eastern United States, including sweetgum (*Liquidambar styraciflua*), black cherry (*Prunus serotina*), blackberry (*Rubus* spp.), and milkweed (*Asclepias* spp.). A more extensive list of bioindicator species is available in an NPS report (Porter 2003), and lists of both sensitive and bioindicator species, by park, are available through the NPS Data Store (https://irma.nps.gov/App/Portal).

Early studies of foliar injury to conifers focused on ponderosa pine and eastern white pine (*Pinus strobus*; Miller and Millecan 1971, Peterson et al. 1991, Peterson and Arbaugh 1992, Pronos and Vogler 1981). Applicability to other coniferous species may vary considerably with respect to specific symptoms and pollutant exposure. Numerous studies have documented the sensitivity of quaking aspen to O_3 under field and experimental conditions (Coleman et al. 1996, Karnosky et al. 1992, Wang et al. 1986), although there is considerable variability in sensitivity among different genotypes (Berrang et al. 1986).

Available plant symptom data are not consistent in suggesting a broadly applicable injury threshold. In general, there may be adverse effects with prolonged exposure to O_3 concentrations greater than about 60 ppb, and there are likely effects with prolonged exposure to concentrations greater than about 80 ppb (Sullivan et al. 2003). Efforts to take results of seedling O_3 exposure studies and scale them up to whole trees have generally not been very successful (Samuelson and Kelly 2001). Trees and seedlings differ in energy budgets, canopy-to-root balance, and P allocation and cannot be assumed to exhibit similar levels of O_3-sensitivity.

Kohut (2007c) evaluated the risk of O_3-induced foliar injury on sensitive plant species in 244 national park units as part of the Vital Signs Monitoring Network. The analysis examined plant response related to O_3 exposure level and environmental conditions. He concluded that 27% of the parks had high risk of foliar injury, 19% moderate risk, and 54% low risk. Parks determined to have high risk included Gettysburg, Valley Forge, DEWA, Cape Cod, Fire Island, Antietam, Harper's Ferry, Manassas, Wolf Trap Farm, Mammoth Cave (MACA), Shiloh, Sleeping Bear Dunes, GRSM, JOTR, Sequoia and Kings Canyon (SEKI), and Yosemite (YOSE).

Because O_3 exposure is episodic and difficult to predict, plant responses may be controlled in large part by the capacity of plants to maintain leaf antioxidant systems throughout the growing season. Burkey et al. (2006) assessed seasonal patterns in ascorbate pool size and redox status in leaves from natural populations of three wildflower species (cutleaf coneflower [*Rudbeckia laciniata* L.], tall milkweed [*Asclepias exaltata* L.], and crown-beard [*Verbesina occidentalis* Walt.]) in GRSM to determine relationships between foliar injury and O_3 exposure. Ascorbic acid is an important metabolite that protects plant leaves from O_3 injury (Conklin and Barth 2004). This was perhaps the first study to characterize leaf ascorbate in natural wildflower populations under field conditions. The three species showed differences in the content of leaf ascorbic acid and oxidation state that corresponded with differences among the three species in foliar symptoms in response to O_3 exposure. Aspects of ascorbic acid metabolism that contributed to plant defense against O_3 injury were identified.

Evans et al. (1996) found that the percent of dead palisade parenchyma cells in plant leaves was positively correlated with the percent of leaf area showing visible O_3 injury. This was found for sassafras (*Sassafras albidum*), cutleaf coneflower, and smooth blackberry (*Rubus canadenis*). Also, the percent of dead cells was positively correlated with cumulative O_3 exposure for sassafras and smooth blackberry.

Research at the Aspen Free-Air Carbon Dioxide Enrichment (FACE) site in Rhinelander, WI, demonstrated that exposure to O_3 can change the composition of plant communities. Aspen clones with high O_3 tolerance were dominant over more O_3-sensitive clones, which showed reduced growth and increased mortality as a result of O_3 exposure. Additionally, O_3 exposure resulted in a competitive advantage for birch and maple over aspen in mixed aspen-birch and aspen-maple communities (Kubiske et al. 2007) with aspen biomass decreasing by 13-23% in response to elevated O_3 over a seven-year study (King et al. 2005). Biomass (above- and below-ground) and net primary productivity (NPP) were measured at the FACE site after seven years of O_3 exposure. Relative to biomass at the control plot, total biomass at the O_3-enriched sites decreased by 23, 13, and 14% in the aspen, aspen-birch, and aspen-maple plant communities, respectively (King et al. 2005). Ozone exposure reduced growth and increased mortality of an O_3-sensitive aspen clone; as a consequence, the tolerant clone became dominant. In mixed aspen birch and aspen-maple communities, O_3 exposure decreased the competitive ability of aspen compared to birch and maple (Kubiske et al. 2007).

Environmental Interactions

Chappelka et al. (1996) judged that the influence of micro-site factors are important in controlling tree species' responses to O_3-induced injury. Available soil moisture appeared to be the most important environmental factor regulating O_3 uptake into foliage, and subsequently effects on plants, through the influence of O_3 on stomatal function. Kohut et al. (2012) found significant O_3 injury on coneflowers in ROMO in surveys conducted from 2006-2010. Risk to vegetation at the park had been rated as low because higher O_3 concentrations that occur during the summer often coincided with dry soil conditions (Kohut 2007c). However, the 2006 to 2010 surveys were conducted in riparian areas, where soil moisture was sufficient to allow the plants to remain physiologically active

and to promote O_3 uptake. Kohut recommended that O_3 surveys in western parks that often experience dry conditions be conducted in riparian or moist areas (Kohut et al. 2012). These riparian areas are also some of the most important areas ecologically in arid regions, supporting high levels of biodiversity.

Ozone may also affect the growth of plants indirectly through interactions with pests and pathogens (Laurence 1981), or by altering the symbiotic relations between plants and associated organisms (Andersen and Rygiewicz 1991, 1995, McCool 1988, Rygiewicz and Andersen 1994, Stroo et al. 1988). The resulting changes in nutrient availability or uptake may also result in altered plant growth, mediated by O_3 exposure (Andersen and Scagel 1997, Weinstein et al. 1991, Weinstein and Yanai 1994). Increased atmospheric concentration of CO_2 and N deposition may increase plant productivity; O_3 exposure may reduce or counteract these effects (Felzer et al. 2004, Ollinger et al. 2002).

Interactions with insects, pathogens, and other pollutants (Bytnerowicz and Grulke 1992) can accentuate the stress complex for plants exposed to O_3. This has been well documented for the effects of O_3 on ponderosa pine. The most common stress complex includes O_3 exposure, drought stress, and bark beetle injury (especially mountain pine beetle [*Dendroctonus ponderosae*] and western pine beetle [*D. brevicomis*]; Pronos et al. 1999, Stolte 1996). This interaction is particularly prominent in the mixed conifer forests of southern California and the southern Sierra Nevada. For example, during the late 1980s and early 1990s, O_3-stressed trees were subjected to several years of low precipitation. This reduced xylem pressure, and many trees were sufficiently weakened that they were susceptible to bark beetles, which proliferated through local and regional outbreaks, resulting in high levels of tree mortality in many areas.

Because lack of adequate soil moisture contributes to decreased stomatal conductance and consequently limits O_3 entry into the leaf tissues (Grulke et al. 2003, Matyssek et al. 2006, Panek and Goldstein 2001, Panek 2004), dry periods exhibit decreased incidence and severity of symptoms of foliar O_3 injury. Such symptoms are therefore not always higher during years having higher atmospheric O_3 concentrations (Smith et al. 2003). The relationship of pollutant exposure to seasonal variation in physiological activity can have a significant influence on O_3 injury in plants (Grulke 1999). The potential for pollutant uptake is higher during periods when plants are most metabolically active. Therefore, at some locations, exposure may contribute disproportionately to injury during the spring when soil moisture and gaseous uptake are higher.

Spatial Patterns in Ozone Effects

Most (244 parks) of the I&M parks in the conterminous United States, plus one in Alaska, were ranked by Kohut (2007b) with respect to overall risk from exposure of vegetation to O_3. This risk assessment was based on the presence of bioindicator plant species, estimated levels of O_3 exposure, and estimated soil moisture conditions during periods of exposure over five years in each park. Each park was assigned a risk ranking of Low, Moderate, or High. These estimated park risk levels are shown in Map 19, and are used in this report as an important part of the basis for estimating spatial patterns in ecological risk in the I&M parks from O_3 exposure. Most of the parks that were classified by Kohut (2007b) as having High risk are located in the eastern United States or in California. The

former group includes MACA, DEWA, and GRSM. The latter includes JOTR, SEKI, and YOSE. The process used by Kohut (2007b) for assigning relative risk was based on:

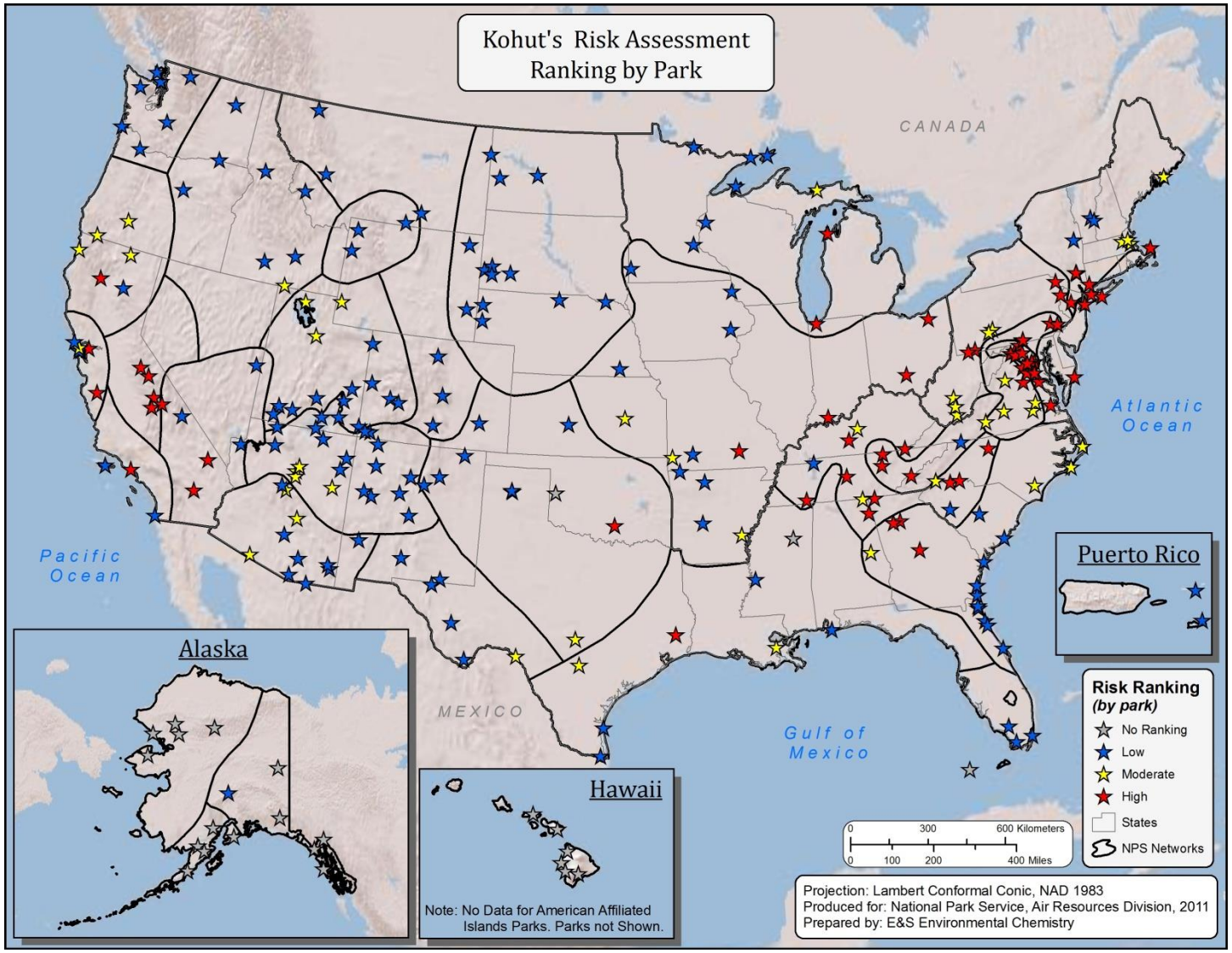
1) the extent and consistency by which the SUM06 and W126 O_3 exposure injury thresholds were exceeded,
2) the nature of the relationship between O_3 exposure and soil moisture, and
3) the extent to which soil moisture levels constrained the vegetative uptake of O_3 during high exposure years.

Kohut (2007b) judged that parks ranked as High are likely to experience foliar injury due to O_3 exposure in most years. A ranking of Moderate suggested that injury is likely to occur at some point during a five-year period. Parks ranked as Low were judged to be unlikely to experience injury during any year.

Kohut's analysis represents a rigorous examination of the major factors known to influence O_3 uptake and injury, and provides the best information to date on risk to plants in parks. However, it was based on data available at the time of the study, from the period 1995-1999. In most areas of the country, O_3 exposures have not significantly changed from that time, so the conclusions are still generally applicable. But to provide more updated information, NPS ARD has developed a simple method for rating current O_3 condition, based on exposure thresholds. This simple method does not take into account environmental factors like soil moisture, so parks should consider their site-specific conditions when reviewing results. For this report, O_3 data from 2005-2009 were examined. These data were used to generate interpolated surfaces of SUM06 and W126-3 mo indices at 10 km resolution (D. Bingham, NPS, unpublished data, 2010). The SUM06 and W126-3 mo index values were determined for each I&M park as a spatially weighted average of all the values that occur within a park. Each was calculated as a three-month average of exposure during the daylight hours. Thresholds for rating condition were based on information from EPA's review of the O_3 standards (2007). The review considered the recommendations of an expert work group (Heck and Cowling 1997) who suggested O_3 thresholds for protecting natural vegetation against foliar injury. Based on these recommendations, the NPS determined that a W126-3 mo $\leq$ 7 ppm-hrs could be considered "good" condition, with impact unlikely, and a W126-3 mo > 13 ppm-hrs would warrant significant concern (NPS 2010). Exposure of W126-3 mo between 7 and 13 ppm-hrs would warrant moderate concern. Equivalent thresholds for the SUM06 index are 8 ppm-hrs and 15 ppm-hrs, respectively (NPS 2010). Thus, the breakdown is as follows:

W126-3mo:
- Good < 7 ppm-hrs
- Moderate Concern 7-13 ppm-hrs
- Significant Concern > 13 ppm-hrs

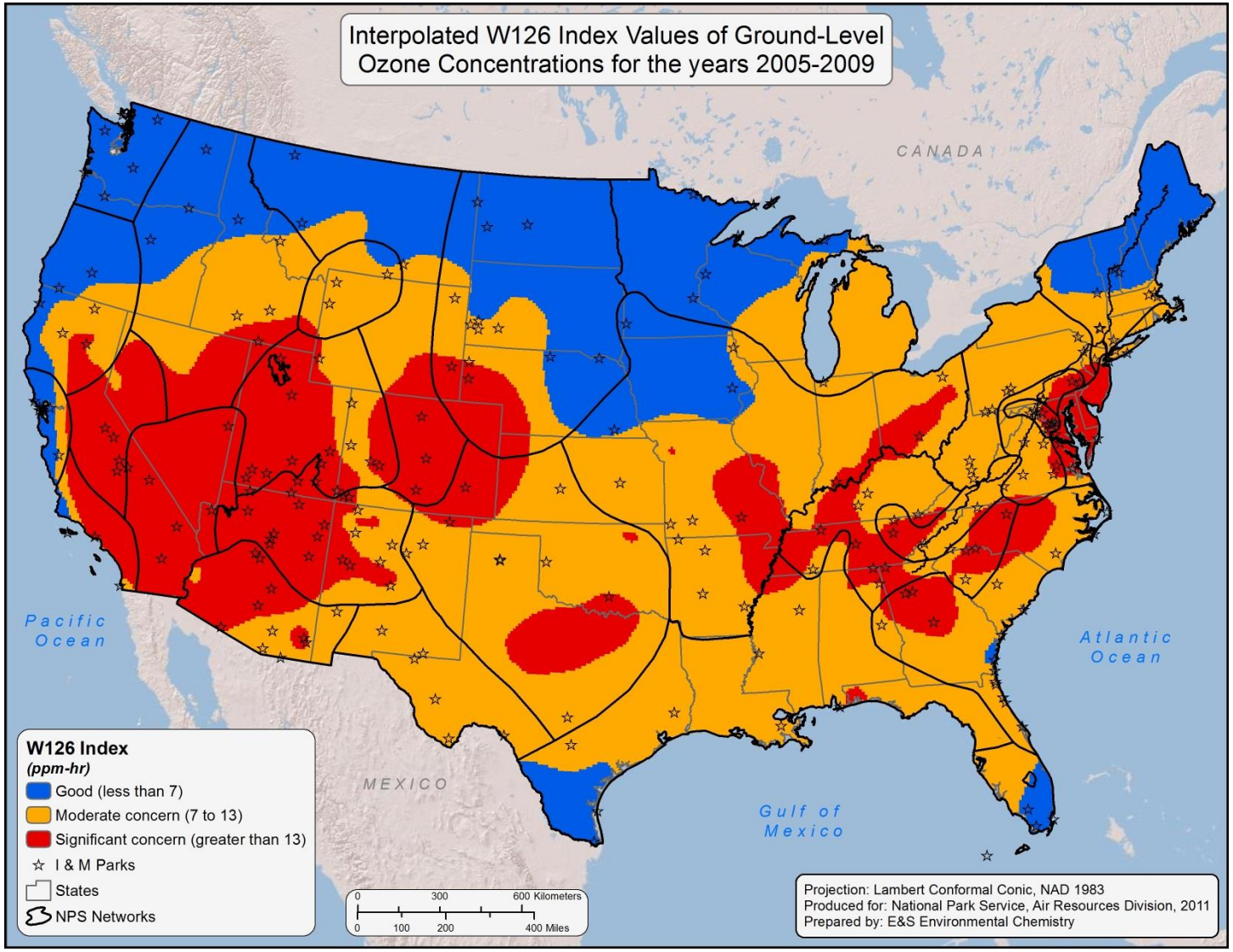
SUM06:
- Good < 8 ppm-hrs
- Moderate Concern 8-15 ppm-hrs
- Significant Concern > 15 ppm-hrs



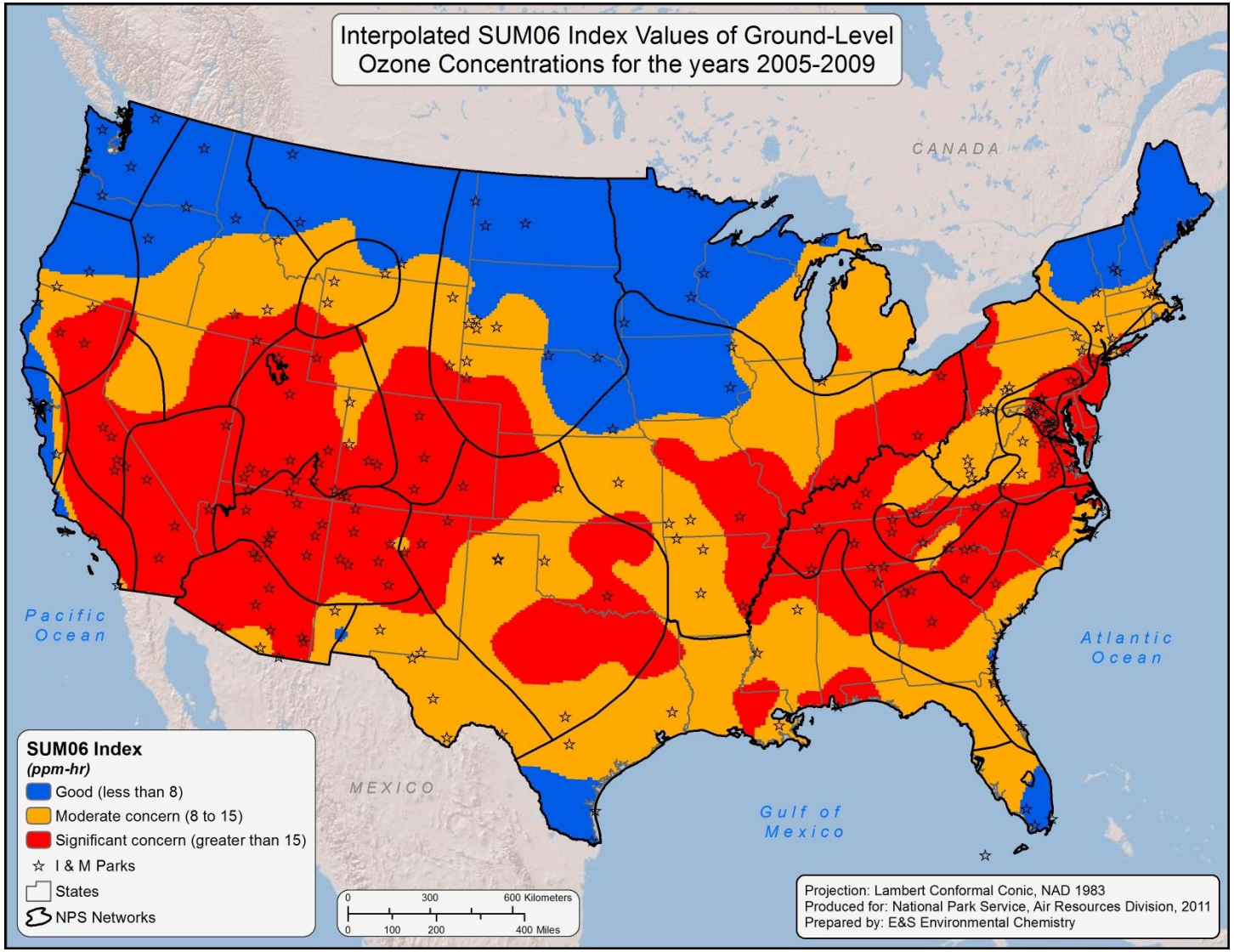
Map 19. Risk ranking for exposure of vegetation in I&M parks throughout the United States to ground-level ozone. (Source of data: Kohut 2007b).

Spatial patterns in estimated cumulative O_3 exposure were similar between the W126-3 mo and SUM06 indices (Maps 20 and 21). However, the areas classified as having High O_3 exposure were somewhat more extensive for the SUM06 index as compared with the W126-3 mo index. Areas classified as having Low O_3 exposure, were nearly identical using the two indices, and included most of the Pacific Northwest, southern Texas, southern Florida, and the northern tier of states except around the eastern Great Lakes region.

Note that there are differences between Kohut's (2007b) risk ranking (Map 19) and the more recent NPS estimates (Maps 20 and 21). In particular, many parks in the arid west were estimated by Kohut to be at relatively low risk even though the exposure indices were relatively high. This difference reflects the low soil moisture conditions in these parks. Thus, there is not always a clear relationship between exposure and risk; low soil moisture limits O_3 uptake, thereby reducing risk. Nevertheless, it is important to recognize that riparian vegetation communities in these arid western parks may, in fact, have sufficiently high soil moisture that risk is enhanced in locally moist areas.



Map 20. Interpolated values of cumulative ozone exposure during the five-year period 2005 through 2009 using the W126-3 mo exposure index.



Map 21. Interpolated values of cumulative ozone exposure during the five-year period 2005 through 2009 using the SUM06 exposure index.

Visibility Impairment

Atmospheric pollutants derived from both natural and human sources can degrade visibility and produce regional haze. In many national parks, this haze impairs the scenic vistas that are integral to a park or wilderness experience. Visibility degradation results from the scattering and absorption of visible light by gases and particles in the atmosphere. If there are no suspended particles in the air, the natural visibility is determined by the amount of light scattered by air molecules. Scattering of visible light from air molecules is called Rayleigh scattering. The light is scattered evenly in both the forward and backward direction, with a preferential scattering of shorter wavelengths; this scattering is responsible for the blueness of the sky. The value of the Raleigh scattering is a function of air density and elevation.

Sources of Visibility Degradation

The natural visibility condition is affected by wildfire, volcanic emissions, wind, biogenic emissions from vegetation, and sea salt aerosols. Research is ongoing to further refine scientific understanding of these natural contributions to visibility impairment.

Particulate matter in the atmosphere, derived from both natural and human sources, also scatters light. The amount of particle light scattering depends on the size and concentration of the particles, which are affected by their physical and chemical properties. Fine particles (particles less than 2.5 µm in diameter) have a greater scattering efficiency on a per mass basis than coarse particles (particles between 2.5 and 10.0 µm in diameter). Particles with sizes near the wavelength of visible light (0.4 µm to 0.7 µm) scatter light most efficiently. Chemical composition of particles also plays a role in their relative light scattering efficiencies. The major categories generally used to differentiate among fine particles that scatter light are SO_4^{2-}, NO_3^-, organics, and soil. Sulfate and NO_3^- aerosols are hygroscopic. In other words, they absorb water when relative humidity (RH) is high. Growth of these aerosols at higher RH conditions can dramatically enhance their effect on light scattering. Coarse particles are generally not speciated and are generally lumped together in terms of their scattering efficiency.

Particulate SO_4^{2-} and NO_3^- are secondary PM species produced in the atmosphere, primarily from gaseous precursors. At sufficiently high humidity levels (RH>85%), they are the most efficient particulate species contributing to haze (U. S. EPA 2009b). Particulate SO_4^{2-} is the dominant source of regional haze in the eastern United States (>50% of the particulate light extinction) and is an important contributor to haze elsewhere in the country (typically >20% of particulate light extinction; U.S. EPA 2009b). Most atmospheric SO_4^{2-} forms from coal-fired power plant emissions.

Particulate NO_3^- is only a minor component of remote-area regional haze in the eastern United States and in the western United States outside California. It is, however, an important contributor to haze throughout most of California and in the upper midwestern United States, especially during winter when it tends to be the dominant contributor to particulate light extinction. Both nitric acid (a reaction product of NO_x emissions) and ammonia (NH_3) are needed to form ammonium nitrate (NH_4NO_3). Urban particulate NO_3^- concentrations are significantly higher than remote-area background concentrations. Particulate NH_4NO_3 concentrations in California and the Midwest are commonly an order of magnitude higher than estimated natural levels of NH_4NO_3. Particulate NO_3^-

concentrations are sensitive to changes in either NO_x emissions (from a combination of mobile and point sources) or NH_3 emissions (principally from agricultural sources).

Elemental carbon (EC) and organic carbonaceous components of PM are responsible for a large fraction of the haze that occurs in many areas. This is especially the case in the northwestern United States (U. S. EPA 2009b). Both EC and organics are products of incomplete combustion of fuels, including gasoline and diesel emissions and smoke from wildland and prescribed fire. Organic PM is also produced by atmospheric transformation of some precursor gaseous emissions. Smoke plume particulates from large wildfires dominate many of the worst haze periods in the western United States. Carbonaceous PM is generally the largest component of urban excess PM smaller than 2.5 μm diameter ($PM_{2.5}$). Western urban areas have more than twice the average concentrations of carbonaceous PM compared with remote areas in the same region. In eastern urban areas, $PM_{2.5}$ is dominated by SO_4^{2-} and carbonaceous components, though the usually high RH in the East causes the hydrated SO_4^{2-} particles to be responsible for about twice as much of the urban haze as that caused by the carbonaceous PM (U. S. EPA 2009b).

$PM_{2.5}$ crustal material (fine soil) and coarse mass (i.e., PM_{10} minus $PM_{2.5}$, where PM_{10} is PM smaller than 10 μm diameter) are significant contributors to haze in the arid southwestern United States where they typically contribute a quarter to a third of the haze. Coarse mass usually contributes twice as much haze as fine soil in this region. Coarse mass concentrations are also high in the central Great Plains. The relative contribution to haze by the high coarse mass in the Great Plains is smaller, however, because of the relatively high concentrations of SO_4^{2-} and NO_3^- PM in that region.

A comprehensive assessment (U.S. EPA 2009b) of the 610 worst sampled haze episodes over a three-year period in the western United States, where dust was the major contributor, categorized each site/sample period into four causal groups: Asian dust, local windblown dust, transported regional windblown dust, and undetermined dust (i.e. not in one of the three other groups). Most dust days occurred at sites in Arizona, New Mexico, Colorado, western Texas, and southern California, and these were dominated by local and regionally transported wind-blown dust (U.S. EPA 2009b). Asian dust caused only a few of the worst dust days during the three-year assessment period, though it was an important source of dust for the more northerly regions of the West and was responsible for 10% to 40% of their worst dust periods.

Organic particulates in the atmosphere are diverse in their makeup and sources. Vegetation itself is an important source of hydrocarbon aerosols. Terpenes, particularly α-pinene, β-pinene, and limonene, released from tree foliage, may react in the atmosphere to form submicron particles. These naturally generated organic particles contribute significantly to the blue haze aerosols formed naturally over forested areas (Geron et al. 2000, U.S. EPA 2004).

Some gases can also absorb light. Nitrogen dioxide is the only major visible light-absorbing gas in the lower atmosphere. It usually does not occur in sufficient concentrations in remote areas to make a major contribution to the total light absorption. Elemental C (soot) is the dominant light-absorbing particle in the lower atmosphere.

Visibility Metrics

To quantify visibility conditions and estimate the degree of degradation caused by various air pollutants, several visibility scales/metrics can be employed. Depending on the application, metrics may include a contrast and color difference index, light extinction coefficient (b_{ext}), visual range (VR), or degree of haziness.

The b_{ext}, often called extinction, represents the attenuation of light per unit distance of travel in some medium, such as air. It is commonly measured in inverse length (e.g., inverse kilometers [km^{-1}] or inverse mega meters [Mm^{-1}]). The b_{ext} reflects attenuation of light due to scattering and absorption of light by aerosols, which include particles and gases in the air. The best possible visibility (particle-free air, or Rayleigh conditions) corresponds to a b_{ext} of approximately 10 Mm^{-1}, although this value is spatially variable.

The b_{ext} is not linear with respect to increases or decreases in perceived visual air quality. For example, a given change in b_{ext} can result in a scene change either unnoticeably small or very apparent depending on the baseline visibility conditions. Therefore, another visibility metric, the haziness index (expressed as deciview [dv]), was defined to index a constant fractional change in the b_{ext} to visual perception (Pitchford and Malm 1994). The haze value in dv is a log-transformation of b_{ext} that provides a perceptually uniform haze metric. The advantage of this characterization is that equal changes in dv are equally perceptible to the human eye across different baseline conditions. Higher haziness index values signify poorer visibility. The EPA has adopted the dv metric for determining progress in improving visibility under the Regional Haze Rule (RHR). The dv is often used in describing overall visibility condition or haze, and in reporting trends in visibility. A 1 dv change would be a small but likely perceptible change in uniform haze conditions, regardless of the baseline visibility level (Pitchford and Malm 1994).

Although the dv is widely used to describe haze conditions and monitor trends in visibility, the b_{ext} is the characterization most used by scientists concerned with assessment of the causes of visibility degradation. Extinction can be directly calculated from light transmittance measurements (measured extinction) or derived from measured atmospheric particle concentrations using linear relationships between the concentrations of particles and gases and their contribution to the extinction coefficient (calculated extinction). Understanding these relationships provides a method of estimating how visibility would change with changes in the concentrations of each of these atmospheric constituents. This methodology, known as "extinction budget analysis", is important for assessing the visibility consequences of proposed pollutant emissions sources or for determining the extent of pollution control required to meet a desired visibility condition (Sullivan et al. 2003). Each haze-causing species in the atmosphere can be measured, and the amount of light extinction that it causes can be calculated at a given location and time.

Uptake of water by fine aerosol particles in the atmosphere has been investigated at remote natural settings, including within several national parks: GRSM, Grand Canyon (GRCA), Big Bend (BIBE; Day and Malm 2001). Inorganic SO_4^{2-} and NH_4^+ salts can absorb water in moist atmospheres. This uptake and release of atmospheric water in response to changes in RH can influence the light scattering properties of aerosols (Day et al. 2000, Horvath 1996, Tang 1996). Light scattering can

increase 2-fold or more at RH above 80% (Day et al. 2000, Rood et al. 1986). Organic C is also an important vehicle for water uptake by atmospheric aerosols (Day and Malm 2001).

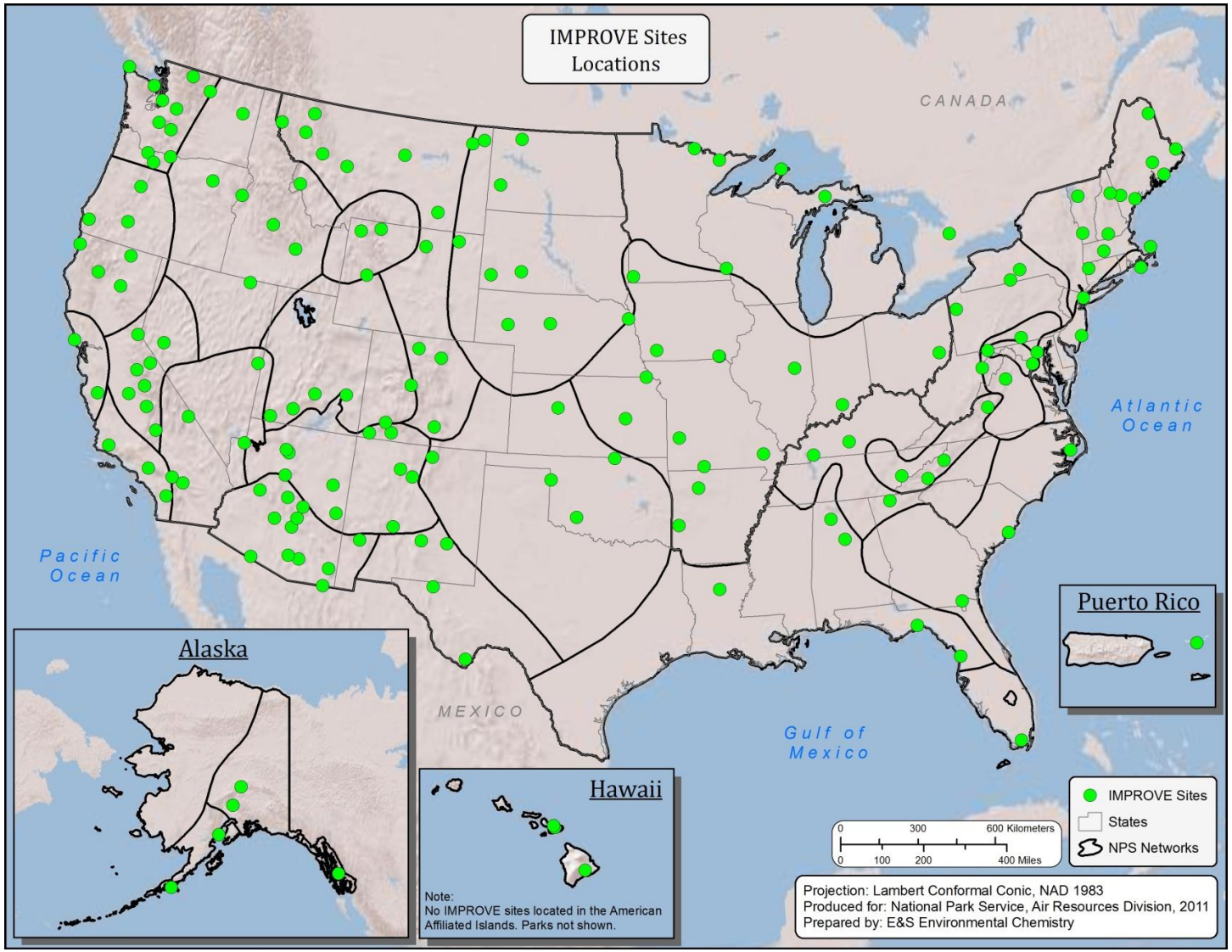
Visibility Monitoring

The Interagency Monitoring of Protected Visual Environments (IMPROVE) Program is a cooperative monitoring effort that is governed by a steering committee comprised of representatives from federal and regional-state organizations. It was established in 1985 to aid in the creation of federal and state implementation plans for the protection of visibility in mandatory Class I areas, as stipulated in the 1977 CAAA. A complete IMPROVE monitoring station includes fine and coarse particle monitoring and optical monitoring, and may have previously also included view monitoring with photography.

The locations of the IMPROVE visibility monitoring sites within each of the I&M park networks are shown on Map 22. Some of these sites are located within national park units; others are located in national forests or at other locations. There are 187 sites included in the IMPROVE database (downloaded from http://vista.cira.colostate.edu/IMPROVE/Default.htm). Fifty-five of these sites are located in national park units, representing 53 individual I&M parks. Average dv values were calculated for some analyses presented in this assessment over a five-year period (2004-2008) for those IMPROVE sites that are located in the I&M parks.

Effects on visibility vary spatially across the United States. Most impairment occurs as regional haze, which is generally most pronounced in the eastern United States and southern California. In the East, ammonium sulfate ($(NH_4)_2SO_4$) contributes at least half of the visibility impairment at most Class I areas, and $(NH_4)_2SO_4$ is a major contributor to visibility impairment throughout the U.S. (Hand et al. 2011). The contribution from NH_4NO_3 is highest in central and southern California and in parts of the Midwest. The contribution from organic C is highest in the Southeast. The contributions from coarse particles and fine soil are highest in the arid southwest (Debell et al. 2006, Hand et al. 2011, U.S. Forest Service et al. 2010).

Since the early part of the 1990s, visibility throughout most remote areas in the conterminous United States has improved substantially. Hand et al. (2014) computed b_{ext} on the haziest 20% of days following RHR guidelines for three major regions: East, Intermountain/Southwest, and West Coast. During the two-decade period 1992 to 2011, the regional mean 20% haziest days decreased by 52% in the East and 20% in the West Coast region, and remained unchanged in the Intermountain/ Southwest region. Improvements for the West Coast region accelerated to -3.5%/yr during the second decade of the monitoring data.



Map 22. Locations of IMPROVE air quality monitoring sites. Also shown are boundaries of park networks.

Particle Monitoring

Particle monitoring provides concentration measurements of atmospheric constituents that contribute to visibility impairment. Four independent IMPROVE sampling modules are used to automatically collect 24-hour samples of suspended particles every 3 days by drawing in air and collecting suspended particles on filters. The filters are later analyzed to determine the chemical makeup of the suspended particles. Three of the four samplers (modules A, B, and C) collect fine particles with diameters <2.5 µm. The fourth sampler (module D) collects particles with diameters up to 10 µm. Module A filters are analyzed to determine the gravimetric mass and elemental composition of the collected particles. Module B filters are analyzed specifically for SO_4^{2-}, NO_3^-, and chloride (Cl^-) ions. Module C filters are analyzed for organic material and light absorbing C. The gravimetric mass of coarse particles (2.5 to 10.0 µm) is determined by subtracting the Module A gravimetric mass from the Module D gravimetric mass.

Optical Monitoring

Optical monitoring provides a direct quantitative measure of b_{ext} that represents overall visibility conditions. Because water vapor in combination with suspended particles can affect visibility, optical stations also record temperature and RH. Optical monitoring uses ambient long-path transmissometers or ambient nephelometers to collect hourly averaged data. Transmissometers measure the amount of light transmitted through the atmosphere over a known distance (between 0.5 and 10.0 km) between a light source of known intensity (transmitter) and a light measurement device (receiver). The transmission measurements are electronically converted to hourly averaged b_{ext} (scattering plus absorption). Ambient nephelometers draw air into a chamber and measure the scattering component of light extinction. Optical measurements of extinction and scattering include meteorological events such as cloud cover and rain, but the data are filtered by flagging as invalid those data points collected under conditions of high RH (>90%). This filtering process is assumed to remove the largest effects of weather from the data set. Optical data also provide concurrent, independent measurement of b_{ext} to compare with calculations made using particle data. Transmissometers have gradually been phased out of the IMPROVE program, due to their relatively high expense compared to nephelometers.

View Monitoring

View monitoring was formerly accomplished with automated camera systems. Cameras typically took three photographs a day (9:00, 12:00, and 15:00) of selected scenes, which formed a photographic record of characteristic visibility conditions. These photographs reveal how differences in visibility affect vistas in a particular park. Based on April, 1995 recommendations of the IMPROVE Steering Committee, view monitoring was discontinued at all NPS Class I areas that had a five-year or greater photographic monitoring record. Webcams have been installed at about 20 parks, and are linked to air quality monitoring stations (http://www.nature.nps.gov/air/WebCams/index.cfm).

Photos of vistas within many of the I&M parks were downloaded for this assessment from http://vista.cira.colostate.edu/IMPROVE/Data/IMPROVE/Data_IMPRPhot.htm. A series of photos representing the best 20%, worst 20%, and annual average visibility were selected. If a photo was not

available for the exact dv value needed to correspond with average haze measurements over the period 2004 through 2008 within a given park, the closest dv photo was selected. All photos in the series were taken at the same time of day.

Regional Haze Rule

In 1977, Congress established a national goal of no human-caused visibility impairment in Class I areas in the year 2064, and in 1999 promulgated a rule requiring states to develop and implement plans to make continuous progress toward that goal. The EPA provided detailed guidance for assessing regional haze (U.S. EPA 2001b). Assessment of progress toward the national goal requires long-term particle monitoring on which to base estimates of natural and current visibility conditions. This long-term monitoring is provided by the IMPROVE Program.

The RHR requires states (and tribes who choose to participate) to review how pollution emissions within the state affect visibility in Class I areas. The RHR also requires states to make "reasonable progress" in reducing any effect that air pollution has on visibility conditions in Class I areas and to prevent future impairment of visibility. The states are required by the rule to analyze a pathway that takes the Class I areas from current conditions to "natural conditions" by 2064. "Natural conditions" is a term used in the CAA, which means that no human-caused pollution can impair visibility. The response to these regulations, while aimed at Class I areas, is expected to improve regional visibility conditions throughout the country.

The RHR requires emissions reductions that will reduce the human-caused contributors to regional haze at 156 of the largest national park and wilderness areas in the United States. The long-term goal is to achieve visibility that represents natural conditions, unimpacted by human-caused emissions, by the year 2064. In order to comply with requirements of the RHR, multistate planning organizations were established, as follows:

- Western Regional Air Partnership (WRAP)
- Central Regional Air Planning Association (CENRAP)
- Midwest Regional Planning Organization (Midwest RPO)
- Mid-Atlantic/Northeast Visibility Union (MANE – VU)
- Visibility Improvement State and Tribal Association of the Southeast (VISTAS)

Each state must describe ambient visibility conditions, based on the best and worst visibility days for the five baseline years 2000 through 2004. Because the IMPROVE sampler operates every 3 days, there are data for about 121 days per year at each site. The 20% highest dv days (approximately 24 haziest days during each year) and the 20% lowest dv days (24 clearest days) are averaged for each baseline year. Each state also must estimate what the 20% worst and best visibility conditions would be like under natural conditions, on days when visibility is only affected by natural emissions sources.

Under the RHR, states must estimate the uniform rate of haze reduction that would allow them to progress from the current conditions to the required natural haze level in 2064. Haze conditions for

this requirement are expressed as the five-year mean of the annual 20% most impaired visibility conditions at each protected Class I area. States also must document that the five-year mean of the annual 20% clearest days does not deteriorate over time at the protected areas.

In order for states to comply with the RHR, they must estimate haze levels at Class I areas that represent the average of the 20% haziest days so that the 60-year uniform rate of progress can be specified. A default approach was described by EPA (2001b) to accomplish that. It was based on the original IMPROVE algorithm (Sisler 1996) for estimating b_{ext}. Thus, EPA provided default estimates of natural background visibility for the mean, clearest, and haziest days for each of the protected areas. States could choose to use these default values or choose to use a refined approach.

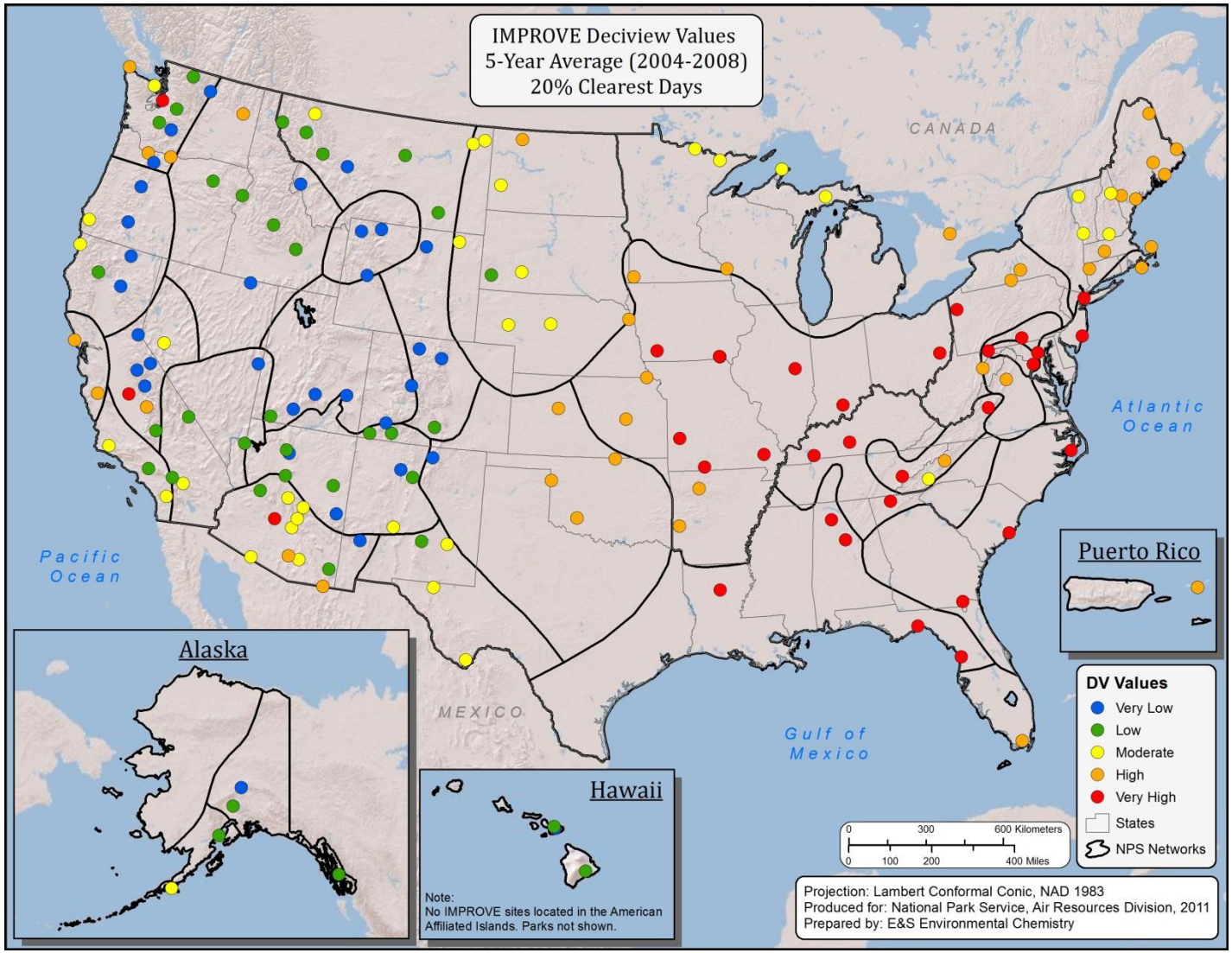
The default approach specified by EPA for estimating natural haze conditions was subsequently reviewed and found to be flawed in multiple respects (Pitchford et al. 2007, Ryan et al. 2005). Problems were identified in the method used to calculate percentiles, and the default approach did not adequately adjust for light scattering by sea salt at coastal locations or the effects of elevation.

The IMPROVE algorithm was revised in 2005 to address some of these problem areas. Use of the revised algorithm for estimating ambient haze also requires use of the same algorithm for estimating natural conditions in order to avoid biasing the calculation of the required uniform rate of progress glide path needed to accomplish the visibility improvements mandated in the RHR. The revised approach is not without problems, however. For example, it assumes two estimates of natural haze-causing atmospheric species concentrations, one for the East and one for the West. As a consequence, there is a rather steep line of demarcation between the East and West in the background haze estimates. There may not be sufficient data to justify breaking down the country into smaller units at this time. Additional research may be needed to further improve the approach for specifying natural visibility conditions.

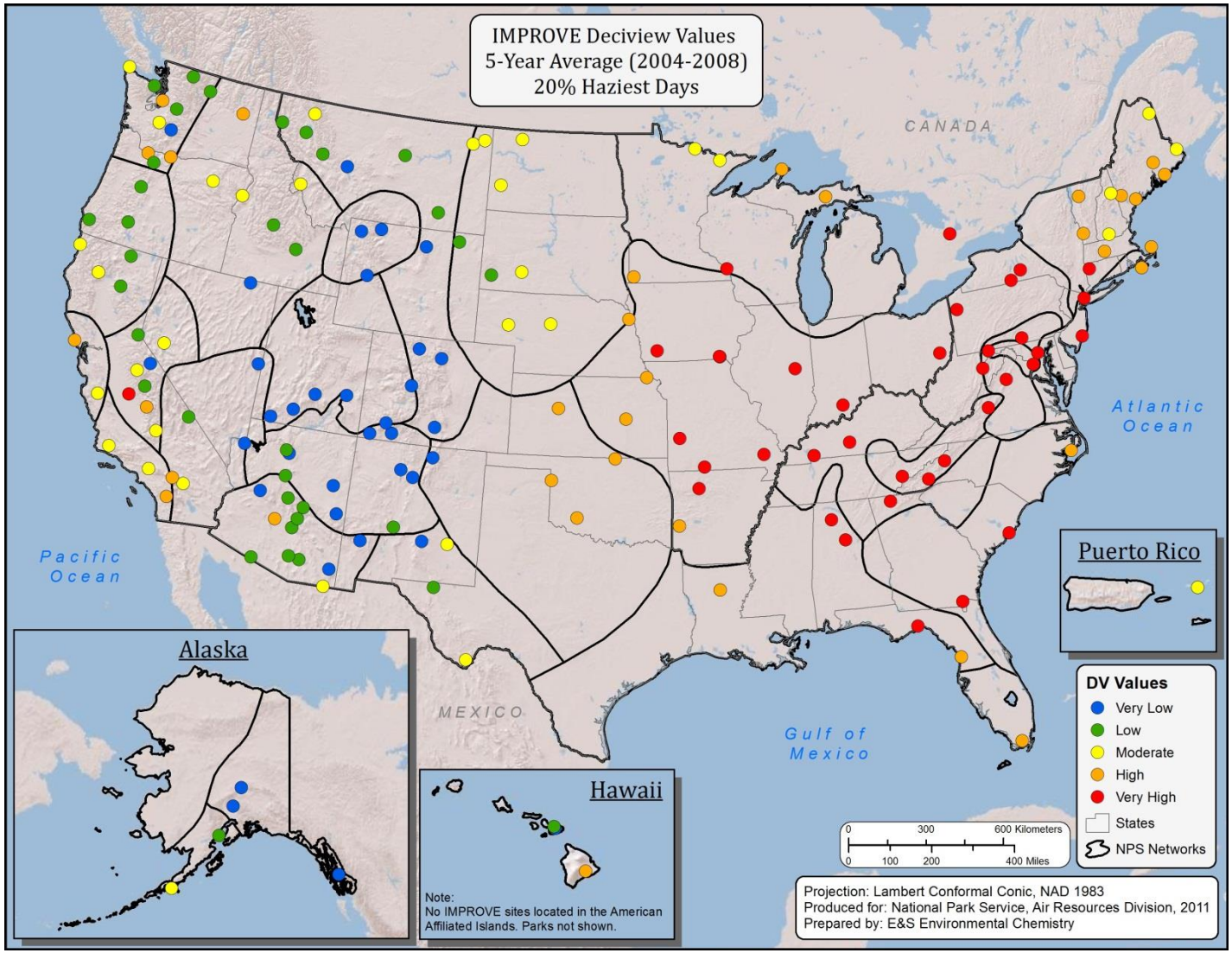
Trends analyses show that over short (2000-2008) and long (1989-2008) time periods, the mass concentrations of major aerosol species have decreased at many IMPROVE sites. These decreasing trends (improving visibility) were largest for the lowest concentrations and during winter seasons, and may not be typical of all sites and species (Hand et al. 2011). However, these results are consistent with 1999-2008 trends at NPS-only sites, which showed larger decreasing trends in dv on the clearest days compared to the haziest days (NPS 2010).

Spatial Patterns in Visibility Impairment

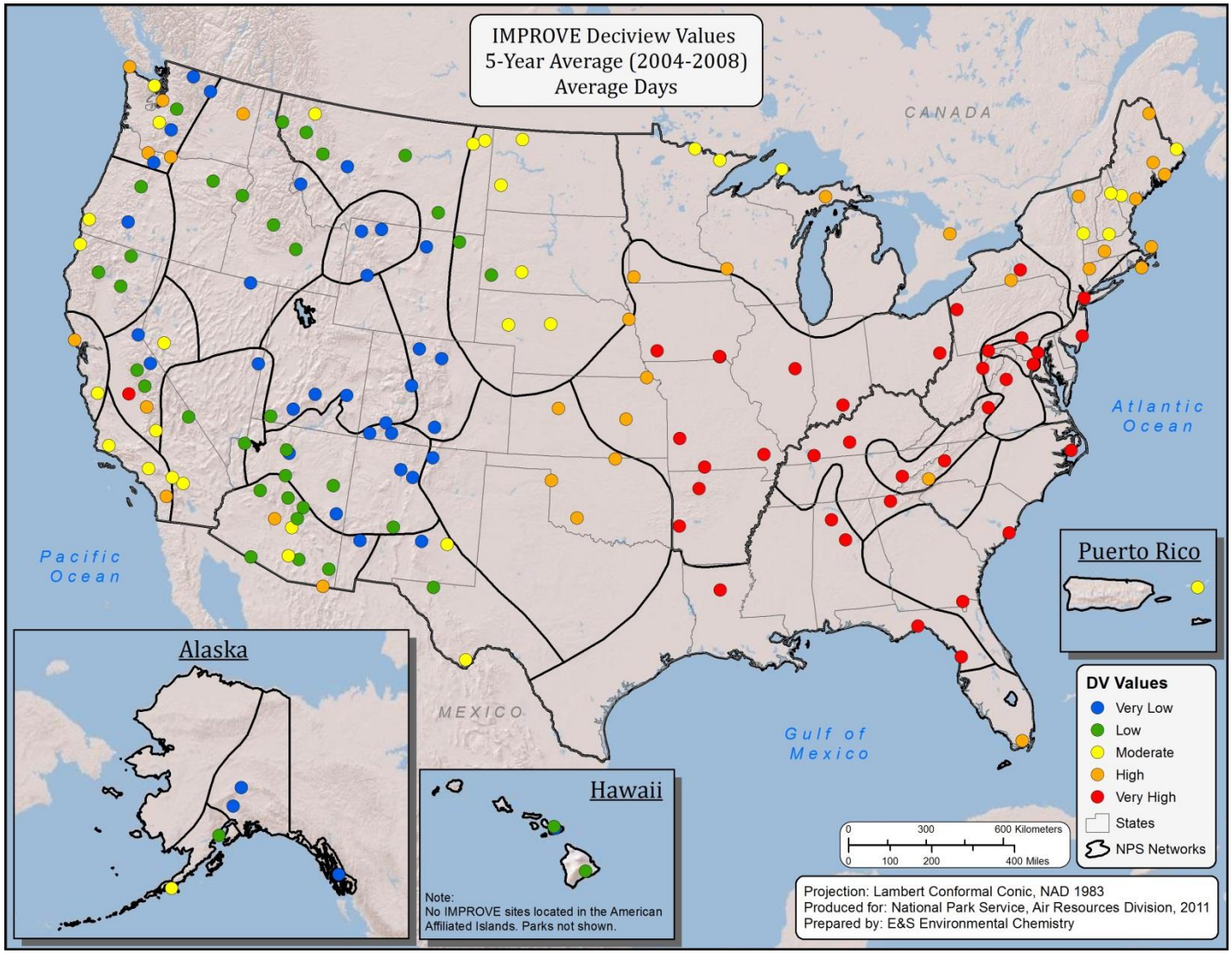
A regional haze dataset was downloaded for this assessment from http://vista.cira.colostate.edu/IMPROVE/Default.htm, based on the revised IMPROVE algorithm. Out of this dataset, measured haze values for the years 2004 through 2008 were extracted. Five-year means of the clearest, haziest, and average 20% visibility days were summarized for the following light extinctions: $(NH_4)_2SO_4$, NH_4NO_3, organic mass, light absorbing C, fine soil, coarse mass, and sea salt.



Map 23. Relative ranking of haze measurements at IMPROVE sites for the 20% clearest days during the five-year period 2004 through 2008. Low dv values correspond to better visibility; as dv increases, visibility decreases.



Map 24. Relative ranking of haze measurements at IMPROVE sites for the 20% haziest days during the five-year period 2004 through 2008 . Low dv values correspond to better visibility; as dv increases, visibility decreases.



Map 25. Relative ranking of haze measurements at IMPROVE sites, based on the average days at each site. Low dv values correspond to better visibility; as dv increases, visibility decreases.

Relative ranking of haze measurement values, expressed in dv, from the IMPROVE sites are provided in Maps 23 through 25 as five-year averages over the period 2004 through 2008. Only sites having monitoring data during the period 2004 to 2008 are included. Results are presented for the 20% of the monitored days having the lowest haze (clearest visibility) at each site (Map 23), the 20% of the days having highest haze (Map 24), and the average 20% days (Map 25). Natural haze is the level of haze expected to occur in the absence of human-caused air pollutants. Ambient haze measurements must be interpreted within the context of estimated natural haze levels. In general, parks that exhibited high levels of ambient haze were also estimated to have relatively high natural haze levels.

In order to rank measured haze values into classes (five classes ranging from Very Low to Very High), dv values for each group were divided using a geometrical interval in ArcGIS. This classification scheme is useful for ranking continuous datasets that are not normally distributed. It creates intervals by minimizing the variance among values within each class and results in classes that contain approximately the same number of parks. The ranking for most sites was based on five years of data.

Extinction budgets are provided in this assessment for each of the park units that contains an IMPROVE monitoring site having data for the time period 2004 through 2008. The contribution of each aerosol type to b_{ext} is shown relative to particulate light extinction, excluding Rayleigh scattering. This approach was taken because the focus of this report is on the components of haze, rather than on all contributors to extinction.

Exposure to Airborne Toxics

Atmospheric emissions of toxic substances can affect resources in parks that are downwind of emission sources, and researchers have become increasingly concerned about the potential susceptibility of resources in the national parks to airborne toxic contaminants. These chemical pollutants can be transported by the wind and deposited on land far from where they originate. Relevant toxic chemicals include Hg, various pesticides, and industrial contaminants, some of which have the potential to bioaccumulate to relatively high concentrations at higher trophic levels of the food web. Combustion products, including other metals and polycyclic aromatic hydrocarbons (PAH), may also be important atmospherically deposited toxic and/or carcinogenic compounds. Adverse effects on sensitive animal species can include reproductive impairment, reduced growth and health, neurological damage, and behavioral changes. Humans consuming contaminated fish and wildlife may also be affected.

Toxic Substances of Concern

The most thoroughly studied airborne toxin that affects park lands is Hg. It is a heavy metal that occurs naturally in several forms. Elemental Hg is released from sources in the earth's crust into the global environment through volcanic and geothermal activity and the weathering of rocks. It is also been emitted by human emissions sources, primarily coal-fired power plants and incinerators. Human-related sources are estimated to account for 50–75 percent of the annual input of Hg to the global atmosphere and, on average, 67 percent of the total Hg in atmospheric deposition to the United States (U.S. EPA 1997b). The most important route of entry of Hg into remote national park

ecosystems is atmospheric deposition of inorganic Hg (Fitzgerald et al. 1998). Once released into the atmosphere, Hg can be deposited to the earth's surface and transformed through natural processes into a toxic form, methylmercury (MeHg; Ullrich et al. 2001), that can bioaccumulate in food webs. Contamination of aquatic ecosystems by Hg has prompted many states to issue fish consumption advisories, and has reduced the benefits provided by fisheries resources in many inland and coastal waters throughout the United States.

The U.S. EPA (1997a) compiled an assessment of the sources and environmental effects of Hg in the United States. A variety of factors were found to influence Hg deposition, fate and transport. Such factors relate in particular to speciation of the Hg that is emitted, the forms in which it is deposited from the atmosphere, and transformations that occur within the atmosphere and within the aquatic, transitional, and terrestrial compartments of the receiving watersheds.

Persistent organic pollutants (POP) constitute another class of potentially toxic contaminants. Many are semi-volatile and therefore are readily emitted and deposited from the atmosphere to the ground surface. They are not readily degraded in the environment and can be concentrated in the food web at higher trophic levels. They can accumulate to toxic levels in piscivorous fish and wildlife, wading birds, and humans. Results of POP biomagnification can include reproductive disruption, neurological disorders, and mortality.

Many POPs have high toxicity, are relatively insoluble in water, and tend to concentrate at each step in the food chain. These compounds include polychlorinated biphenyls (PCBs), dioxins, dichlorodiphenyltrichloroethane (DDT) and its breakdown products, chlordane, dieldrin, endosulfan, PAH, and others. Although the use of many of these compounds is now restricted, their presence in the environment has human health, environmental, and economic impacts (Clair et al. 2011). Flame retardants, developed and deployed to respond to stricter fire regulations are also of increasing concern. For example, levels of polybrominated diphenylether (PBDE) flame retardants have increased dramatically in smelt in the Great Lakes (Chernyak et al. 2005).

Mechanism of Exposure

Mercury

Atmospheric Hg deposition increased with industrialization. For example, Steinnes et al. (2005) found that Hg concentrations in dated peat samples were about 15 times higher in deposits from the last 100 years as compared with deposits laid down during pre-industrial times. However, the complexities of atmospheric Hg chemistry and the typically low atmospheric concentrations make quantification of Hg deposition difficult (Lynam and Keeler 2005).

The cycling of Hg in natural ecosystems is complex. Deposited Hg(II) can revolatilize back to the atmosphere, be methylated in the soil, or be transported to a water body via runoff and leaching. Methylation can also occur within the water body, and either Hg(II) or MeHg can be reintroduced from the water back to the atmosphere. Mercury deposited to the O horizon of the soil can be strongly retained, and then re-emitted to the atmosphere with burning (Dicosty et al. 2006).

Mercury in vegetation is derived almost exclusively from the atmosphere (Grigal 2003). Mercury uptake from soil is limited, partly because plants transport Hg to foliage very poorly (Grigal 2002). Grigal (2003) provided a review of the sequestration of Hg in forest and peatland ecosystems. A fundamental aspect of Hg cycling is its strong relationship to organic matter. For that reason, peatlands sequester much larger quantities of Hg than would be expected on the basis of their land area. As a consequence, peatlands constitute important sources of Hg exposure.

Although any form of Hg can be considered toxic, the greatest threat to the environment, wildlife, and people is low-level exposure to an organic form of Hg: MeHg. Methylmercury is a persistent bioaccumulative toxin that is formed when certain bacteria convert inorganic Hg into MeHg. MeHg can enter through the digestive systems of animals and bind to proteins. It bioaccumulates as each successive predator in the aquatic food chain consumes higher concentrations of MeHg. Low levels of MeHg in surface water (less than about 1 part per trillion) can bioaccumulate over a million-fold and reach toxic levels in fish (Driscoll et al. 2007). Predatory fish, piscivorous birds, and mammals (including humans) that eat contaminated fish can be exposed to toxic levels of Me-Hg.

In anaerobic environments in wetlands and lake or stream sediments, Hg(II) can be methylated to MeHg, which biomagnifies and bioaccumulates in aquatic food webs (Hall et al. 2005, Wiener et al. 2003). Sulfate-reducing bacteria are largely responsible for production of MeHg from inorganic Hg (Compeau and Bartha 1985, Gilmour et al. 1992). Thus, atmospheric S deposition is an important driver of Hg methylation and subsequent biomagnification. Relatively low concentrations of inorganic Hg in surface water can contribute to substantial Hg bioaccumulation in aquatic ecosystems when and where environmental conditions favor methylation, which is largely carried out by SO_4^{2-}reducing microbes. Organic MeHg is among the most toxic and widespread environmental contaminants that affect aquatic ecosystems within the national parks (cf., Brumbaugh et al. 2001).

Persistent Organic Pollutants

Important organic atmospheric contaminants deposited in national parks are generally those that are transported long distances in the atmosphere, are subsequently deposited into remote locations, and are bioaccumulated to sufficient levels that they can impact humans, fish, or wildlife (Swackhamer and Hornbuckle 2004). Certain physical and chemical properties facilitate the movement of these contaminants from land and water surfaces into the atmosphere, provide stability, and enhance accumulation in lipids. The smaller PAH compounds differ in that they degrade relatively rapidly in the atmosphere or at the surface subsequent to atmospheric deposition.

Most POPs enter the environment via human activities, including synthetic pesticide application, emissions of polychlorinated dibenzo-p-dioxins (PCDDs) from incinerators, and accidental release of PCBs from transformers (Lee et al. 2003). Once they are introduced into the environment, their accumulation and magnification in biological systems are determined by physiochemical properties and environmental conditions. Many of these pesticides are carcinogenic or estrogenic and pose potential threats to aquatic and terrestrial biota.

Spatial patterns in exposure and effects of air toxics in national park units throughout the United States are not well known. To better understand atmospheric transport and the potential risks to

national park resources of atmospheric emissions of toxic substances, the NPS initiated the WACAP in 2002 (Landers et al. 2010). Composed of a team of multidisciplinary researchers, WACAP was charged with determining the presence, identity, method of accumulation, contamination indicators, sources, and effects of airborne contaminants in 8 core national parks and 12 secondary national parks in the western United States, extending from Alaska south to the Sierra Nevada and Rocky Mountains.

Hageman et al. (2006) reported results of analysis of snow samples collected in seven western national parks and analyzed for CUPs and historic-use pesticides (HUPs). The most frequently detected CUPs were dacthal, chlorpyrifos, endosulfan, and γ-hexachlorocyclohexane. The authors concluded that agricultural practices were largely responsible for the distribution of pesticides in snow in many of the surveyed national parks. In the Alaskan parks, however, pesticide deposition was attributed to long-range atmospheric transport. In other parks, the percent of the total pesticide deposition attributable to regional sources was associated with regional cropland occurrence and the vapor pressure and atmospheric half-lives of the pesticides (Hageman et al. 2006). Among the parks studied, percent regional transport was highest for SEKI, GLAC, and ROMO, and lowest for MORA and the parks in Alaska. Percent regional, as opposed to long-range, transport was highest for dacthal and dieldrin due to their low vapor pressures and short half-lives in air.

The WACAP study concluded that local sources, such as nearby agricultural and industrial activity, are more likely than global sources to control atmospheric deposition of CUPs and HUPs in most national parklands. Contaminant deposition in Alaska, which has few nearby industrial or agricultural sources, must be attributed to atmospheric transport from outside the region (Landers et al. 2010).

Use of flame retardants has increased in recent decades due to fire product safety regulations. Some flame retardant chemicals are toxic and are readily transported atmospherically. Use of some has been banned in Europe and parts of the United States because of their persistence and tendency to bioaccumulate (Hoh et al. 2006).

PAH include hundreds of different compounds that are characterized by possessing two or more fused benzene rings. They are widespread contaminants in the environment, and are formed by incomplete combustion of fossil fuels and other organic materials. Eight PAH are considered carcinogenic and 16 are classified by EPA as priority pollutants. The behavior of PAH is strongly determined by their chemical characteristics, especially their nonpolarity and hydrophobicity. They readily adsorb to particulates in the air and to sediments in water. Srogi (2007) provided a review of PAH concentrations in various environmental compartments and their environmental risks and possible effects on ecosystems and human health.

The PAH contaminant group includes common air pollutants in metropolitan areas, derived in part from vehicular traffic. Other sources, in addition to gasoline and diesel combustion, include Al production industries, wood heating, forest fires, prescribed fires, and various forms of fossil fuel combustion (Sanderson et al. 2004). Analysis of WACAP data found that elevated levels of PAHs in

GLAC were traced to a nearby aluminum smelter, whereas sources to other national parks ranged from local point sources to diffuse regional and global sources (Usenko et al. 2010).

Experiments have shown a variety of adverse effects from exposure of animals to POPs, especially PCBs, PCDDs, and polychlorinated dibenzofurans (PCDFs). Observed effects have included fetal deformities, DNA mutations, immune suppression, neurobehavioral effects, and cancer (Clair et al. 2011, Pohjanvirto and Tuomisto 1994).

Biomagnification

Biomagnification is the progressive accumulation of chemicals with increasing trophic level (LeBlanc 1995). It describes the process of chemical accumulation in the food chain. Pollutants that biomagnify accumulate in body fat and become more concentrated at each level of tropic transfer. Organic (methylated) Hg is the most likely metal to biomagnify, in part because organisms can efficiently assimilate MeHg and it is slowly eliminated (Croteau et al. 2005, Reinfelder et al. 1998).

Atmospheric emissions of SOCs and metals are of interest primarily because of their detrimental effects on biota, particularly the more sensitive species that can be found in remote national parks. The WACAP study showed significant biomagnification of these pollutants in all parks studied; fish showed SOC concentrations that were 5 to7 orders of magnitude higher than concentrations in abiotic components sampled (air, snow, and water). Concentrations of PAH, CUPs, and hexachlorocyclohexanes (HCHs) tended to be highest in vegetation, whereas fish tissue accumulated mostly PCBs, chlordanes, DDT, and dieldrin.

The bioavailability of MeHg in the environment is also of particular importance to humans who can accumulate high levels of MeHg from eating contaminated fish. Avoiding exposure to Hg is particularly important for pregnant women and nursing mothers. Mercury poisoning can cause neurological impairment in children, leading to effects on memory, visual and spatial ability, information processing, and general intelligence (Mahaffey 2005).

Because atmospheric Hg must be methylated in order to bioaccumulate in the food web, significant efforts have been made to understand the bacteria responsible for this chemical transformation. Sulfate-reducing bacteria have been shown to be the main agents of Hg methylation in sediments (Gilmour et al. 1992) and wetlands (Branfireun et al. 1999, St. Louis et al. 1994), although Fe-reducing bacteria can also be important. In ecosystems that are SO_4^{2-}-poor, the total amount of biologically-available S controls the activity of these bacteria, and thereby the rate of MeHg production. Atmospheric SO_4^{2-} deposition, leading to the stimulation of SO_4^{2-}-reducing bacteria and increased Hg methylation may have caused or contributed to the observed post-industrial amplification of MeHg concentrations in fish (Jeremiason et al. 2006). Studies have demonstrated increased levels of MeHg production with experimental addition of SO_4^{2-} (Branfireun et al. 1999, Gilmour and Henry 1991, Gilmour et al. 1992, Jeremiason et al. 2006). In addition, fish have shown increased MeHg burdens in acidified lakes as compared with non-acidified lakes receiving similar atmospheric Hg deposition (Gilmour and Henry 1991). Therefore, reduced SO_4^{2-} emissions and deposition may be expected to cause a corresponding reduction in Hg methylation and bioavailability (Jeremiason et al. 2006).

The WACAP analyzed salmonid fish tissue for contaminants and biomarkers to assess fish condition. Vitellogenin (Vtg) concentration was also analyzed as a biomarker indicating exposure to estrogen and estrogen-mimicking chemicals. Many SOC contaminants have been shown to be endocrine disrupting compounds (EDCs) that interfere with natural hormonal regulation (e.g. dieldrin, PCBs, endosulfan, DDT, PAH, etc.). The levels of Vtg in male fish can constitute a helpful biomarker for indicating the presence of these contaminants.

In order to evaluate possible human health concerns due to biomagnified contaminant concentrations in fish, the WACAP study sampled for contaminant concentrations 136 fish from 14 lakes in the 8 core parks and compared their findings with EPA's *Guidance for Assessing Chemical Contaminant Data for Use in Fish Advisories*. They found that over half of study fish (77) in 11 of the lakes exceeded subsistence fishing human health thresholds for concentrations of the contaminants dieldrin and/or p,p-DDE. Nine of the lakes demonstrated mean fish dieldrin and p,p-DDE that exceeded human contaminant health thresholds for subsistence fishing. These EPA thresholds were not exceeded by any other SOC contaminant concentrations in fish.

High concentrations of contaminants in fish can be detrimental to piscivorous wildlife. The Hg burdens in fish at many WACAP sites exceeded published health thresholds for mink, river otter, and belted kingfisher. Although production of DDT was banned in the United States in 1972, concentrations of the DDT and its byproducts in fish remained above the health threshold for kingfisher at two sites in SEKI and one in GLAC. Dieldrin concentrations in fish did not exceed the wildlife health thresholds in any of the parks. Dieldrin production in the United States was banned in 1987, following a 1974 ban of the pesticide for agricultural use. ROMO contained fish with the highest dieldrin concentrations of any park, which may have resulted from production of dieldrin in Denver between 1952 and 1982.

For lakes studied in WACAP, fish in Burial Lake in the arctic Noatak National Preserve (NOAT) bioaccumulated the highest concentration of Hg. The other arctic lake sampled (Matcharak Lake) also contained fish with comparatively high Hg concentrations. Snow, sediments, and vegetation in these parks showed low Hg concentrations, suggesting that the high Hg concentrations found in fish were a result of other characteristics of the watershed, such as efficient transformation of atmospheric Hg into methyl Hg, the form that can bioaccumulate through the food web. These two arctic lakes both showed fish with Hg concentrations that were too high for human consumption, as defined by the EPA contaminant health threshold.

Plant foliage can accumulate elemental Hg over time in response to air and soil exposure (Ericksen et al. 2003, Frescholtz et al. 2003). Foliar/air Hg exchange has been shown to be dynamic and bi-directional (Millhollen et al. 2006). These investigators compared foliar Hg accumulation over time in three tree species with fluxes measured using a plant gas-exchange system subsequent to soil amendment with mercury chloride ($HgCl_2$). Root tissue Hg concentrations were strongly correlated with soil Hg concentrations, suggesting that below-ground accumulation of Hg by roots may be an important process in the biogeochemical cycling of Hg in soil systems. Nevertheless, measured foliar Hg fluxes indicated that deposition of atmospheric Hg constituted the dominant flux of Hg to the leaf surface (Millhollen et al. 2006).

Persistent organic pollutants can move in successive steps of evaporation, atmospheric transport, and deposition towards colder areas. This is called cold condensation; it can be responsible for high concentrations of POPs in remote arctic and alpine regions (Blais et al. 1998, Simonich and Hites 1995), including in some western national parks. These POPs can then accumulate and biomagnify at higher levels of the food web, eventually potentially impacting fish and wildlife reproduction, behavior, growth, and mortality.

Effects of Atmospherically Deposited Toxic Substances

Effects on Fish

Increased body burdens of Hg in fish can lead to decreased reproductive success and behavioral alterations. Yellow perch are often studied as a primary indicator species for Hg contamination in the environment. Ecological effects thresholds for Hg concentration in fish prey have been proposed at levels lower than human health thresholds.

Mercury concentrations in fish were generally lower at WACAP sites (in the western United States) than in fish from lakes in the midwestern and northeastern United States. Nevertheless, concentrations in fish from some WACAP lakes exceeded EPA thresholds for human consumption.

Histopathological biomarkers provide evidence regarding the effects of toxins on individual organisms. One such biomarker is the macrophage aggregate, a focal accumulation of macrophages in the spleen, kidney, or liver of fish that indicates an immune system response to environmental conditions. The macrophage aggregates are formed in response to tissue damage (Schwindt et al. 2008). Significant correlations have been found between increased macrophage aggregates in fish from polluted waters and fish exposed to Hg or other metals (Capps et al. 2004, Fournie et al. 2001, Handy and Penrice 1993, Khan 2003, Manera et al. 2000, Meinelt et al. 1997). Schwindt et al. (2008) demonstrated an association between Hg and trout kidney and spleen tissue damage, as indicated by increased macrophage aggregate occurrence. This research was conducted on four species of trout collected from 14 lakes in the WACAP national parks or preserves in the western United States. This result suggests that Hg and/or other contaminants might adversely impact fish that inhabit remote and protected lakes in western national parks. Some "intersex" fish (male and female reproductive structures in the same fish) were found in ROMO and GLAC, but not in any of the other six parks sampled in the WACAP study. The causes and consequences of this reproductive disruption remain to be determined (Schwindt et al. 2009).

Effects on Humans

The U.S. EPA recently conducted the National Study of Chemical Residues in Lake Fish Tissue, a screening-level survey of chemical residues in fish throughout the conterminous United States. Sampling sites were selected using a random approach, and results are therefore applicable to numbers and percentages of lakes regionally and nationally. The focus was on identifying chemical concentrations in fish that were above levels of potential concern for humans and piscivorous wildlife (Table 15). Fish tissues were analyzed for 268 persistent, bioaccumulative, and toxic chemicals, including Hg, PCB congeners, dioxins and furans, and a variety of pesticides and other SOCs (U.S. EPA 2009a). These pollutants have been delivered to fish in the sampled lakes from both

atmospheric and non-atmospheric sources. Over a sampling period of four years, 486 predator fish fillets and 395 bottom-dwellers (whole body analysis) were analyzed from 500 sampling locations. Results were extrapolated to an estimated 76,559 lakes for predators and 46,190 lakes for bottom-dwellers. Mercury and PCBs were detected in fish collected from all sampled lakes; dioxins and furans were detected in 81% of the predator fish samples and 99% of the bottom-dweller samples. Other contaminants in fish were not as widely distributed.

Table 15. Numbers and percentages of lakes, from among 76,559 target lakes in the conterminous United States, that had predator fish species having chemical concentrations above screening values for protecting human health, based on a survey by EPA of fish in 500 lakes.

		Lakes Above Human Health Screening Values	
Chemical	**Screening Value**	**Percent of Population**	**Number of Lakes**
Mercury	0.3 ppm	48.8	36,422
PCBs	12 ppb	16.8	12,886
Dioxins and Furans	0.15 ppt	7.6	5,356
DDT	69 ppb	1.7	1,329
Chlordane	67 ppb	0.3	235

Analyses of predator fish fillets indicated that nearly half (36,422 lakes) of the sampled population had Hg tissue concentrations that exceeded the Hg human health screening value of 0.3 ppm. Nearly 17% of the sampled population had PCB tissue concentrations above the 12 ppb human health screening value. Smaller percentages of the sampled lakes exceeded screening values of dioxin and furan concentrations, DDT, and chlordane.

Data from the WACAP study showed that average Hg levels in lake trout from Alaska's NOAT were above the guidelines established by EPA. Mercury levels in other species of fish collected at Gates of the Arctic, OLYM, MORA, and SEKI national parks also exceeded the EPA thresholds. In 3 of the 8 parks assessed (ROMO, SEKI, GLAC) concentration of the pesticide dieldrin was detected in some fish at levels above EPA's human cancer risk threshold for recreational fish consumption. Dieldrin concentrations in fish at all national parks, except Olympic, exceeded human health thresholds for subsistence fish consumption. Average DDT (i.e., p,p'-DDE) concentrations in fish exceeded the human cancer risk threshold for subsistence fishers at SEKI lakes and Oldman Lake in GLAC (Landers et al. 2010).

Flanagan-Pritz et al. (2014) analyzed fish pesticide data collected in 14 national parks in Alaska and the western U.S. The analysis found that concentrations of some historic-use pesticides exceeded EPA guidelines for human subsistence fish consumers at 13 of 14 parks. Eagles-Smith et al. (2014) examined over 1,400 fish across 21 national parks in the western U.S. They found that total Hg

concentrations in 68% of the fish sampled were above exposure levels recommended by the Great Lakes Advisory Group as being unsuitable for unlimited consumption by humans.

All 50 states issued Hg advisories for human fish consumption in 2008 (Fenn et al. 2011). That represented an increase in lake area under advisory of 19% and an increase in river length under advisory of 42% compared with 2006. Mercury advisories for coastal waters increased by 25% from 2004 to 2008. These increases were likely due mainly to increased availability of measured data, rather than increases in Hg deposition or methylation (Fenn et al. 2011). The U.S. EPA (2001a) recommended a human health criterion of 0.3 ppm in fish and shellfish tissue to protect the general population. More stringent restrictions may be appropriate for women of child-bearing age and children. Some states, including Maine and Minnesota, use a more restrictive human health standard of 0.2 ppm in fish.

Effects on Piscivorous Wildlife

Methylmercury causes damage to the vertebrate central nervous system. Embryos are the most sensitive life forms of vertebrates (Clarkson 1992, Scheuhammer 1991). Low-level dietary Hg exposures that cause no measureable effects on adult birds can impair egg fertility, hatchling survival, and reproductive success (Scheuhammer 1991). In reproducing females of fish, birds, and piscivorous mammals, MeHg passes directly to developing egg or embryo (Evers et al. 2003, Hammerschmidt and Sandheinrich 2005, Heinz et al. 2010). These early life stages are more sensitive than adults to the adverse effects of MeHg exposure (Evers et al. 2003, Scheuhammer et al. 2007, Wiener et al. 2003).

Eagles-Smith et al. (2014) found that in 21 western U.S. national parks, total Hg concentrations in 35 percent of fish sampled exceeded a benchmark for risk to highly sensitive fish-consuming birds. Flanagan-Pritz et al. (2014) found that historic-use pesticides exceeded USEPA guidelines for wildlife (kingfisher) health thresholds at 13 of 14 parks in the western U.S. and Alaska.

In piscivorous birds, including loons and bald eagles, Hg poisoning can lead to brain lesions, reduced reproductive success, increased chick mortality, spinal cord collapse, and neuromuscular problems. The common loon (*Gavia immer*) has been widely used as a Hg bioaccumulation indicator for risk to piscivorous birds (Evers et al. 2008, Evers et al. 2011b). It is listed as threatened in Michigan and as a species of special concern in New York and Wisconsin. Because loons feed almost exclusively on fish and crayfish and are relatively long-lived, they can bioaccumulate a substantial amount of Hg (Evers et al. 2011a). Nevertheless, common loons are considered less sensitive to Hg than some other piscivorous birds. They do, however, concentrate Hg in their blood to levels that are high enough to impair reproduction at some locations (Burgess and Meyer 2008, Evers et al. 2011b). Belted kingfisher (*Ceryle alcyon*) has also been used as an indicator of Hg pollution. Kingfishers are piscivorous and widely distributed, occurring in many national parks, including many of the WACAP parks. Lazorchak et al. (2003) developed fish Hg contaminant thresholds for kingfishers; these thresholds were exceeded in nearly all fish in all WACAP lakes (Landers et al. 2010). Average concentrations of Hg in fish in many parks studied by WACAP exceeded risk thresholds for health impacts to fish-eating birds and mammals (Landers et al. 2010).

Reproductive effects on fish-eating birds have been reported at fish Hg levels of 0.16 ppm (Fenn et al. 2011). Methylmercury concentrations are sometimes also relatively high in song birds that feed on aquatic insects.

Mink (*Neovison vison*) has been proposed as a sentinel species indicating toxic contaminant exposure (Basu et al. 2007, Martin et al. 2011). This species constitutes a good candidate for biomonitoring due to its wide distribution and abundance, upper level trophic status, and availability of tissue samples from trappers (Mason and Wren 2001). Symptoms of Hg toxicity in mink include decreased coordination, loss of weight, and splaying of hind legs (Wobeser et al. 1976, Wren et al. 1987). River otter (*Lutra canadensis*) is also widely distributed and a good indicator of Hg contamination. Hg levels in fish from WACAP lakes often exceeded the health thresholds (Lazorchak et al. 2003) for both mink and river otter (Landers et al. 2010).

As more research has been conducted during the last few decades, high concentrations of Hg have been increasingly documented in more species of wildlife, especially across the Great Lakes region and into the northeastern United States. Recent research has also decreased estimates of effects levels, suggesting sublethal effects on wildlife (including effects on reproduction and biochemical processes) at whole-fish concentrations of 0.2 to 0.3 ppm (Beckvar et al. 2005, Dillon et al. 2010, Sandheinrich and Wiener 2011).

Spatial Patterns in Exposure to Toxic Substances

The WACAP study focused on SOCs and metals, largely because of their capacity for atmospheric transport over long distances. Semivolatile organic compounds can undergo repeated volatilization on surfaces, such as plant foliage, in response to diel changes in temperature. As a consequence, such compounds can be deposited, re-emitted, and re-deposited multiple times. This behavior can cause these compounds to move large distances in a leap-frog fashion. The SOCs were classified into four groups: CUPs, North American HUPs, industrial/urban use compounds (IUCs), and combustion byproducts. WACAP identified and analyzed over 100 SOCs representing various levels of volatility, solubility in water, hydrophobocity, and persistence in the environment. In each of the core parks, a variety of ecosystem components were sampled, including air, snow, water, sediments, lichens, conifer needles, and fish, to identify concentrations and potential biological impacts of contaminants. Air, lichens, and conifer needles were analyzed in the 12 secondary parks. WACAP also used back-trajectory cluster analysis in the core parks to spatially model atmospheric transport of these air pollutants (Landers et al. 2010).

Mercury

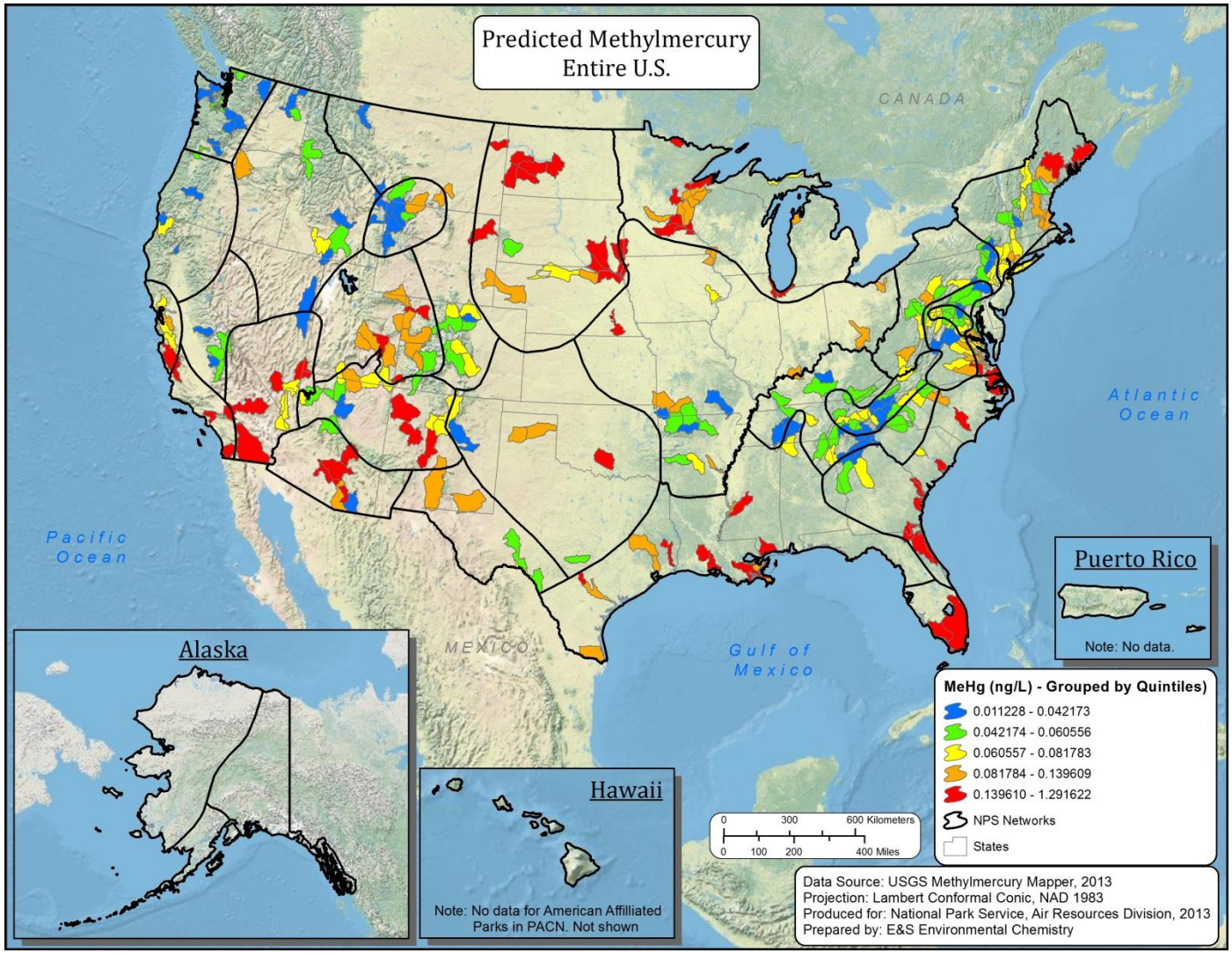
Spatial patterns in I&M park sensitivity to potential damage from Hg exposure across the United States can be evaluated using maps of interpolated wet Hg deposition and Hg methylation potential. Uncertainty is high in both cases. Wet deposition data are currently available from the MDN at monitoring sites across the United States. The spatial coverage of the monitoring data are too sparse in some regions to allow rigorous interpolation of site-specific measurements, but the MDN does provide interpolations for much of the United States. These data reflect only wet deposition. Dry Hg deposition data are not available regionally. To evaluate likely patterns in atmospheric Hg deposition across the I&M parks, we used wet Hg deposition estimates for 2011 from MDN (Map 9). In general,

wet deposition of Hg is highest in Florida, the Gulf States, and north into the Heartland. High deposition also occurs in mountainous areas, including the Rockies, Sierra Nevada, and Cascades, reflecting the higher levels of precipitation in those areas. Wet Hg deposition tends to be lower in the West (at lower elevations), Upper Midwest, Northeast, and Mid-Atlantic regions. Although dry deposition estimates are not available for most areas, limited research indicates that dry deposition can equal or exceed wet deposition, especially in arid regions. In areas of New Mexico, estimated dry Hg deposition was about 60% of total (wet+dry) deposition (Caldwell et al. 2006).

USGS (Last modified February 20, 2015) predicted surface water MeHg concentrations for all hydrologic units included in an NPS I&M Program unit where sufficient empirical data were available to generate a prediction. Watershed boundaries based on eight-digit hydrologic unit codes (HUCs) were selected for data aggregation due to the hydrologically relevant nature of Hg cycling and ecosystem sensitivities (Seaber et al. 1987). Predictions were generated using a partial least squares (PLS) regression model, with input parameters selected based on literature consensus.

Twelve datasets representing water-quality sampling sites from across the conterminous U.S. were compiled by USGS (Last modified February 20, 2015), representing various projects having surface water data for pH, SO_4^{2-}, and organic C together with MeHg. Methylmercury analyses for all data were performed by the Wisconsin Mercury Research Laboratory. Predictions of MeHg were made using regression on four selected independent variables: pH, SO_4^{2-}, total organic C (TOC), and watershed percent wetland. PLS is a shrinkage method in which a continuous portion of the information contained in linear combinations of the variables (components) is used for regression. Leverage calculations indicated that TOC had the most importance relative to the other parameters in describing the variability of MeHg concentration. Predicted MeHg concentrations were obtained by applying the (HUC-level) prediction dataset to the PLS model. Total Hg concentrations were not included in the calibration of the model. Therefore, this model represents only the potential sensitivities of ecosystems to surface-water MeHg contamination (USGS Last modified February 20, 2015) providing that sufficient quantities of inorganic Hg are available for methylation.

Predicted MeHg concentrations in surface waters varied across the conterminous United States, based on USGS (2012) estimates for eight-digit HUCs containing I&M parklands (Map 26). Geographic hotspots containing relatively high estimates of MeHg occurred throughout the southeast coastal region, upper midwest, intermountain and desert southwest, and northern New England. Estimated MeHg concentrations tend to be lower in the interior mid-Atlantic region, northern Rocky Mountains and Great Plains, and Pacific Northwest. The results of this analysis should be considered a first approximation of risk. Sampling of biota in areas of high predicted MeHg can confirm whether bioaccumulation in the food web is occurring. WACAP researchers recommended sampling fish in areas of concern, because bioaccumulation of contaminants in fish puts them at risk for adverse effects, as well as the species that eat them (birds, wildlife, humans). In some areas it may be more appropriate to sample songbirds, insects, amphibians, or mammals (Landers et al. 2008).



Map 26. Predicted MeHg concentrations in surface waters throughout the conterminous United States by HUCs that contain national parklands. Estimates were generated by USGS (Last modified February 20, 2015). Rankings are based on quintile distributions across all I&M parks having estimates by USGS.

Semi-Volatile Organic Compounds

Within the WACAP monitoring effort, the highest pesticide concentrations in snow were found in the Rocky Mountains in GLAC and ROMO, and in the California Sierra Nevada Mountains (SEKI). Pesticide concentrations in vegetation were highest in California (SEKI and YOSE) and in the Rocky Mountains (GLAC and Great Sand Dunes [GRSA]); for other ecosystem components, including fish, these same parks often exhibited the highest measured total pesticide concentrations (Landers et al. 2010).

At the WACAP parks having high vegetation contamination, the major SOC pollutants were the CUPs endosulfan and dacthal. Contaminant concentrations generally increased with elevation, so high elevation areas in parks may be at extra risk for contamination; PAH was an exception, decreasing at higher elevation, which may have been a result of increased wildfires and human activity at lower elevation. Dieldrin, an acutely toxic pesticide that causes reproductive impairment in fish (http://www.chem.unep.ch/gpa_trial/11aldi.htm), was measured at significantly higher concentrations in fish at some WACAP sites (particularly SEKI, GLAC, and ROMO) than in comparable ecosystems in Canada. Proximity of cropland was a statistically significant indicator of the presence of pesticides in WACAP parks. In parks in the contiguous United States, CUP concentrations in snow and vegetation were strongly correlated with percent of cropland within 150 km of the park. In Alaska, there are no croplands within 150 km of the WACAP sample sites; therefore, presence of pesticides was assumed to result from long-range atmospheric transport and deposition (Landers et al. 2010).

HUPs that are now prohibited in the United States were found at higher concentrations in the lower 48 states than in Alaska, suggesting continued persistence, despite the fact that they are no longer used in this country. Regulations on emissions appear to have been effective in reducing contamination from some airborne pollutants. High-temperature fossil fuel combustion causes increased atmospheric deposition of Cd, Pb, and spheroidal carbonaceous particles. Historical records of these contaminants show peak deposition around the 1960s and a significant decline in recent decades, probably in part due to regulation of Pb content in gasoline and requirements of the CAA.

In an analysis of fish from 14 parks in Alaska and the western U.S., Flanagan-Pritz et al. (2014) (2014) found that SOC contaminant loadings were highest in fish from Alaskan and Sierra Nevada parks. Historic use contaminants were highest in Alaskan parks, while CUPs were higher in the Rocky Mountains and Sierra Nevada.

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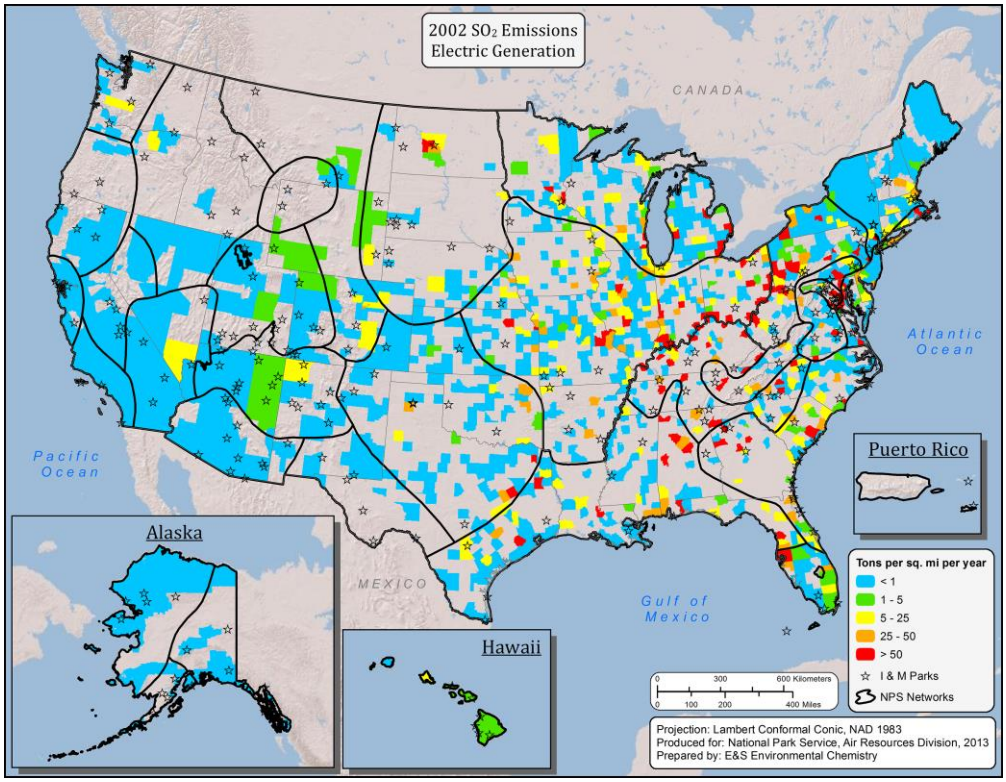
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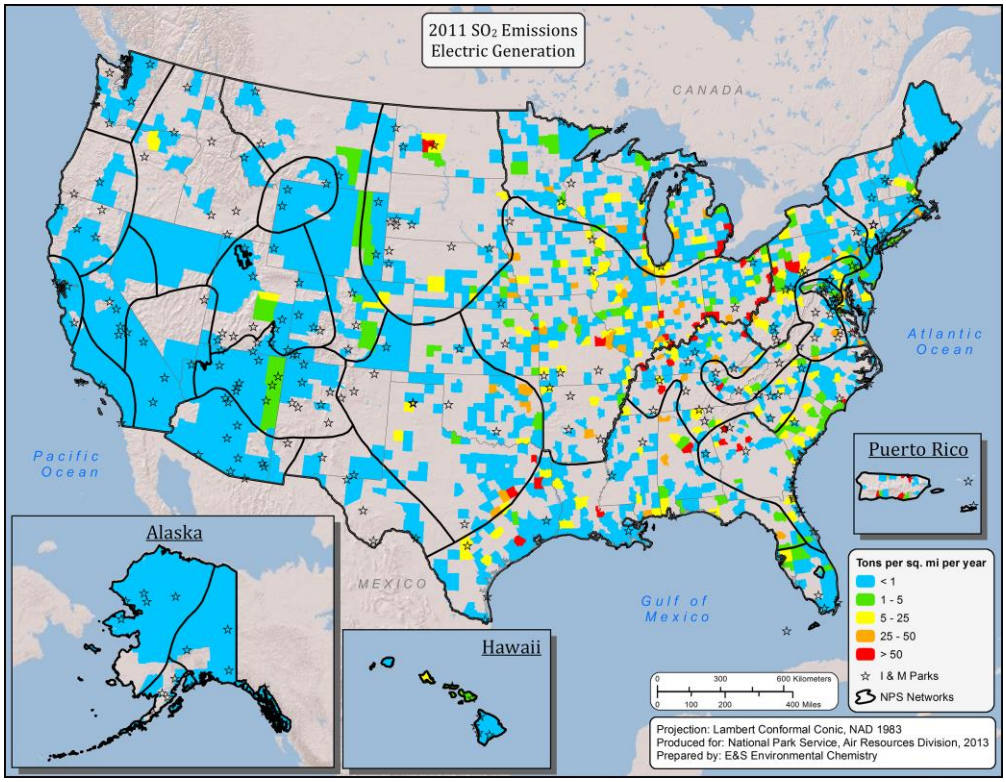
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Appendix A: Maps showing breakdown of emissions, by source sector, for SO_2, NO_x, and NH_3 sources

a)

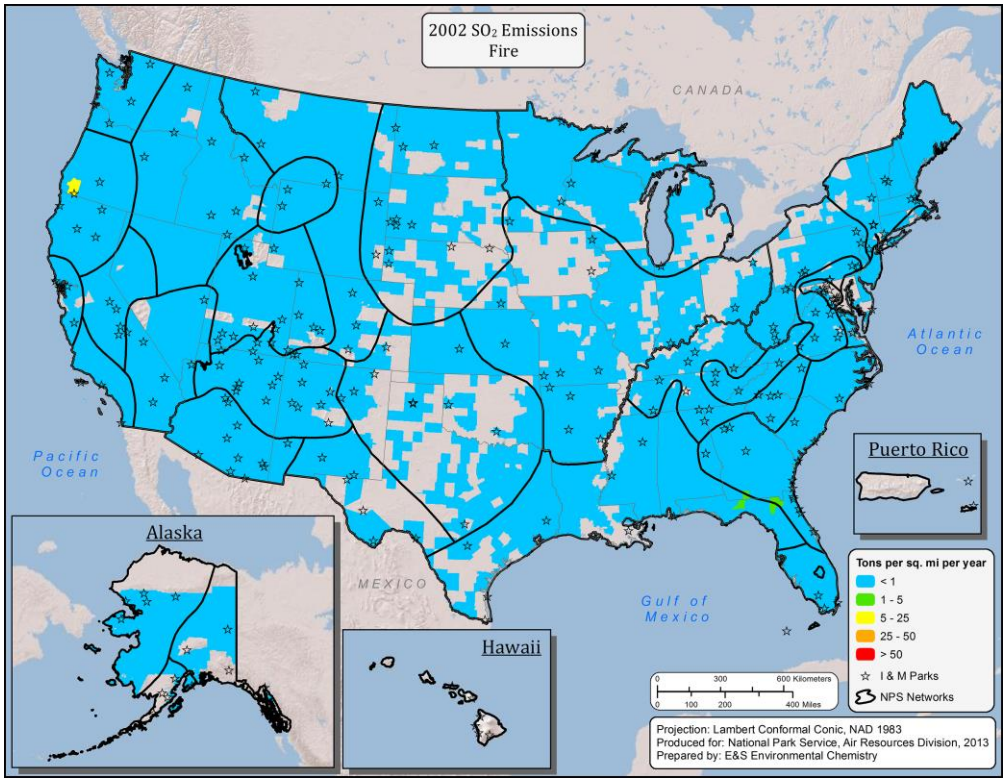


b)

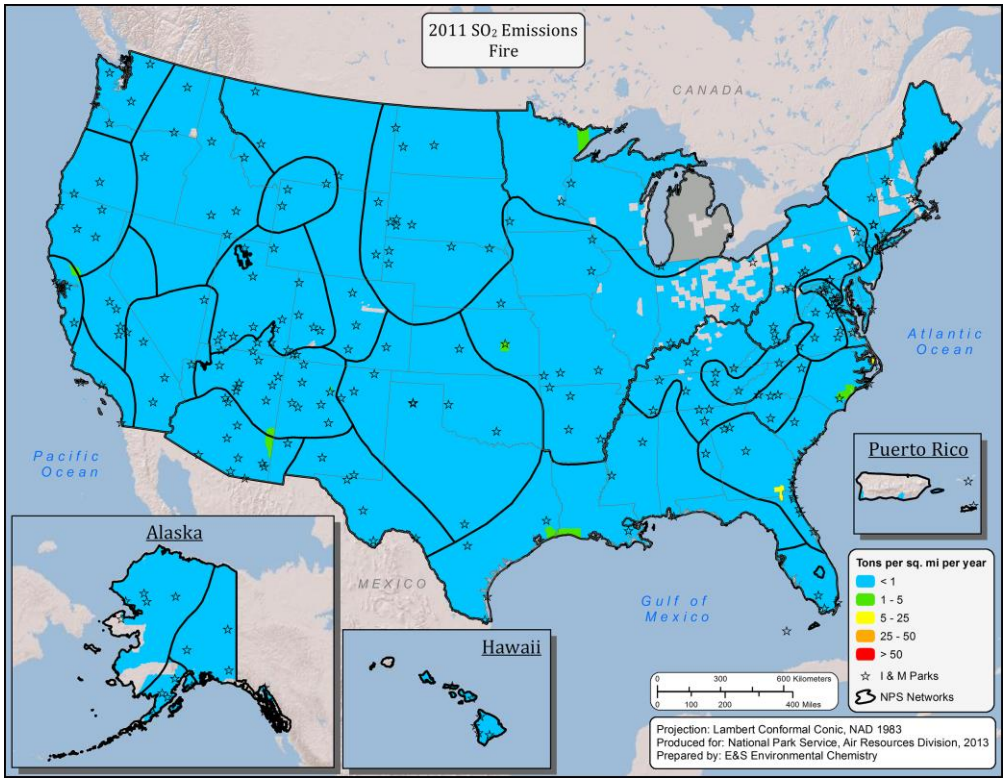


Map A-1. Total SO_2 emissions, by county, attributable to the electricity generation sector, for the years a) 2002 and b) 2011, based on data from the NEI.

a)

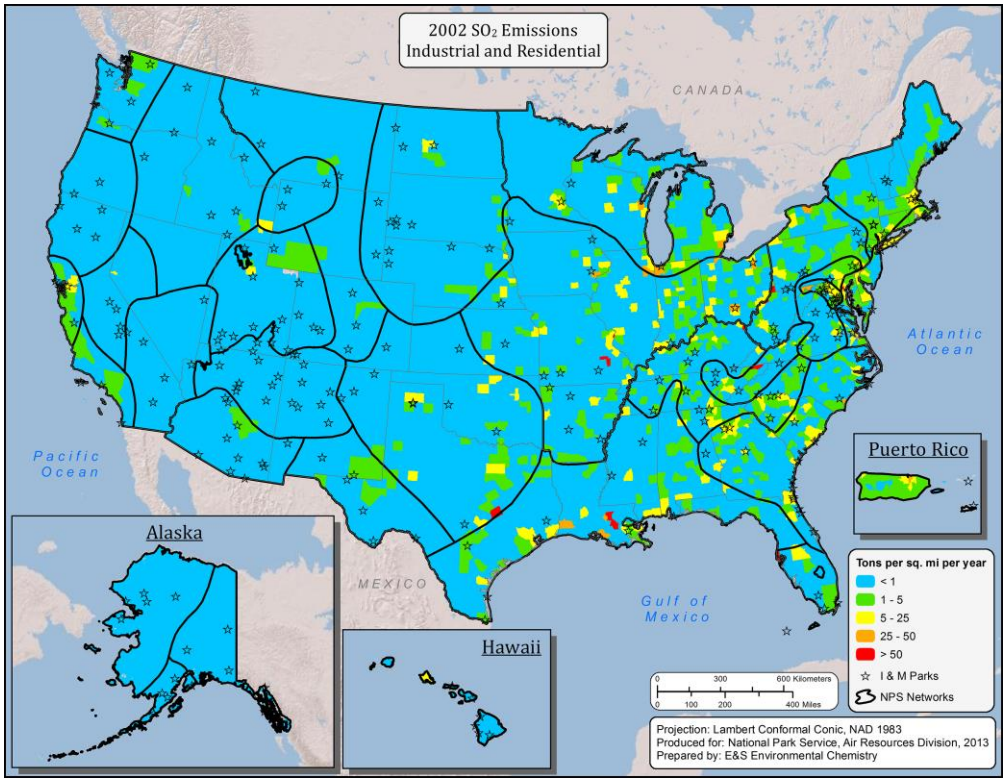


b)

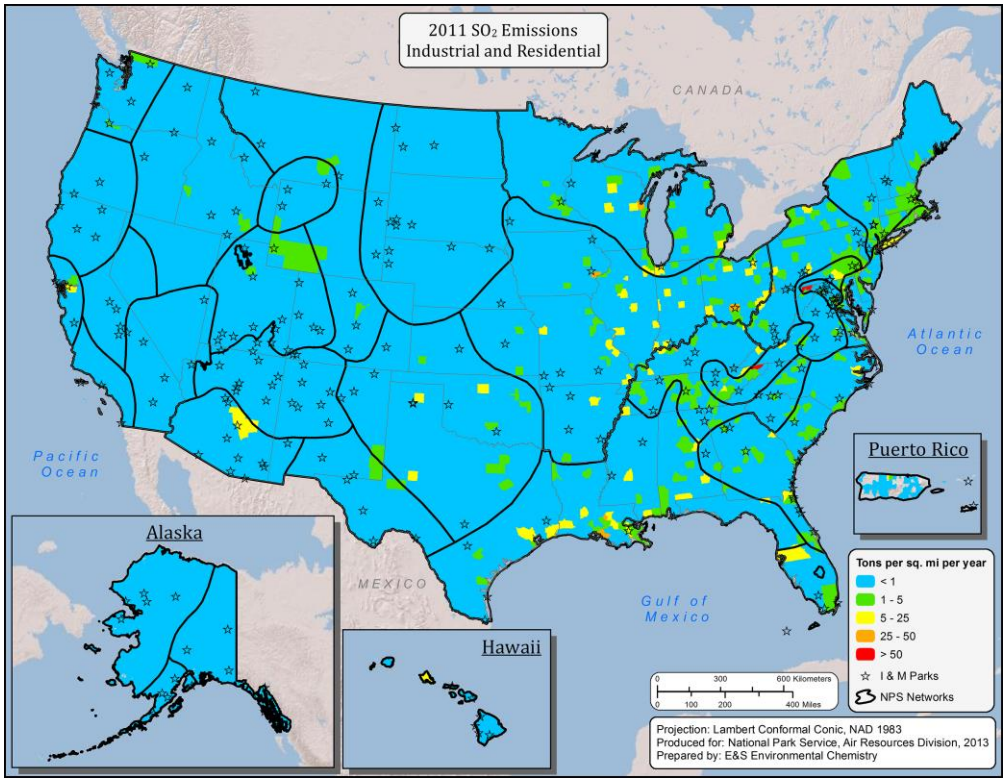


Map A-2. Total SO_2 emissions, by county, attributable to fire, for the years a) 2002 and b) 2011, based on data from the NEI.

a)

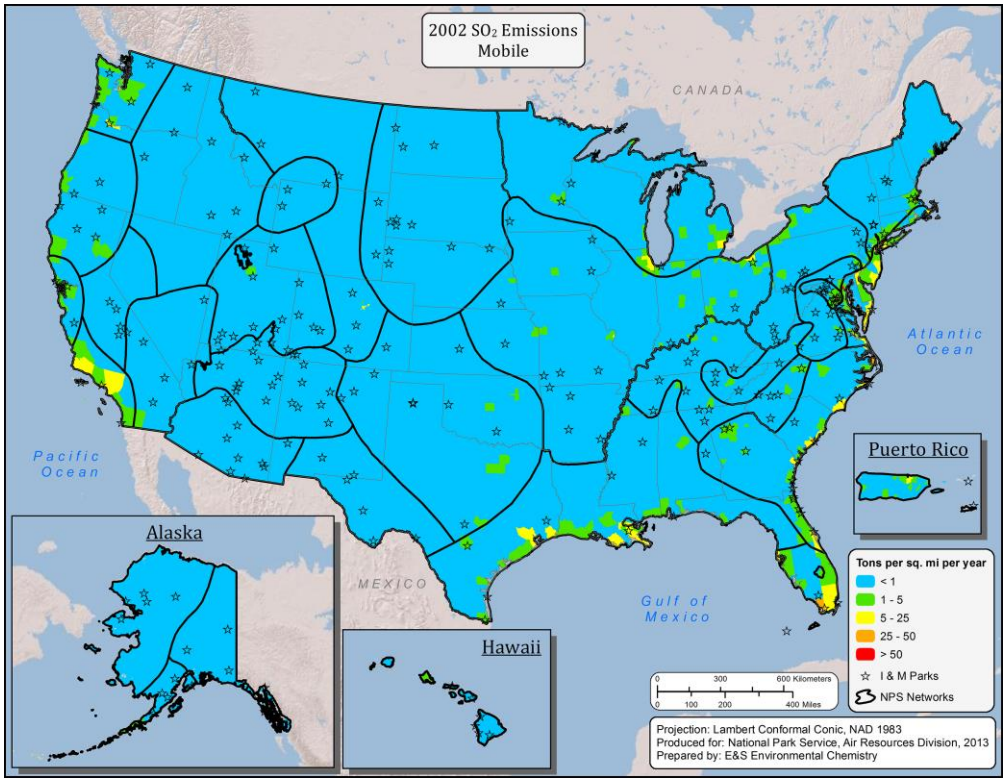


b)

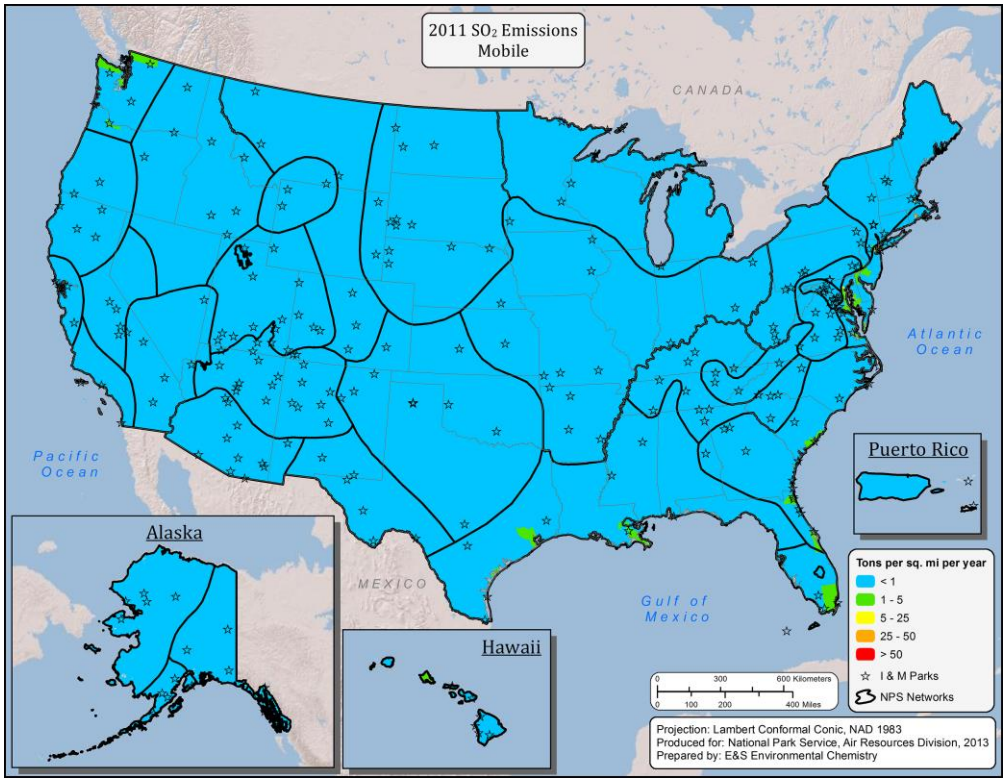


Map A-3. Total SO_2 emissions, by county, attributable to the industrial and residential sector, for the years a) 2002 and b) 2011, based on data from the NEI.

a)

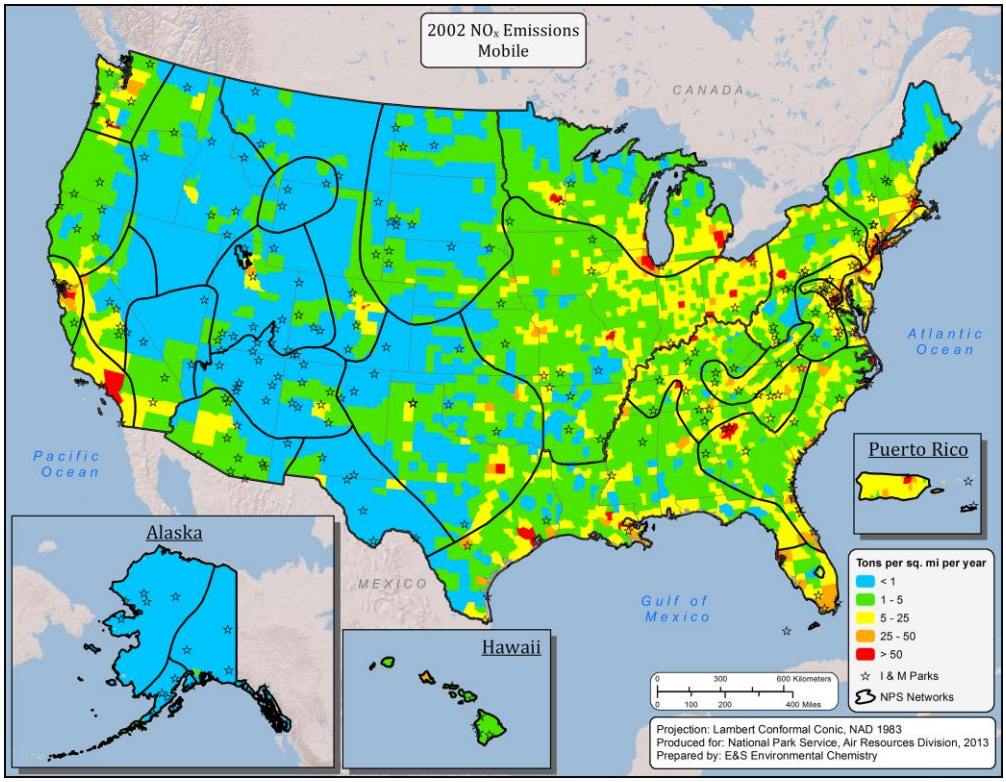


b)

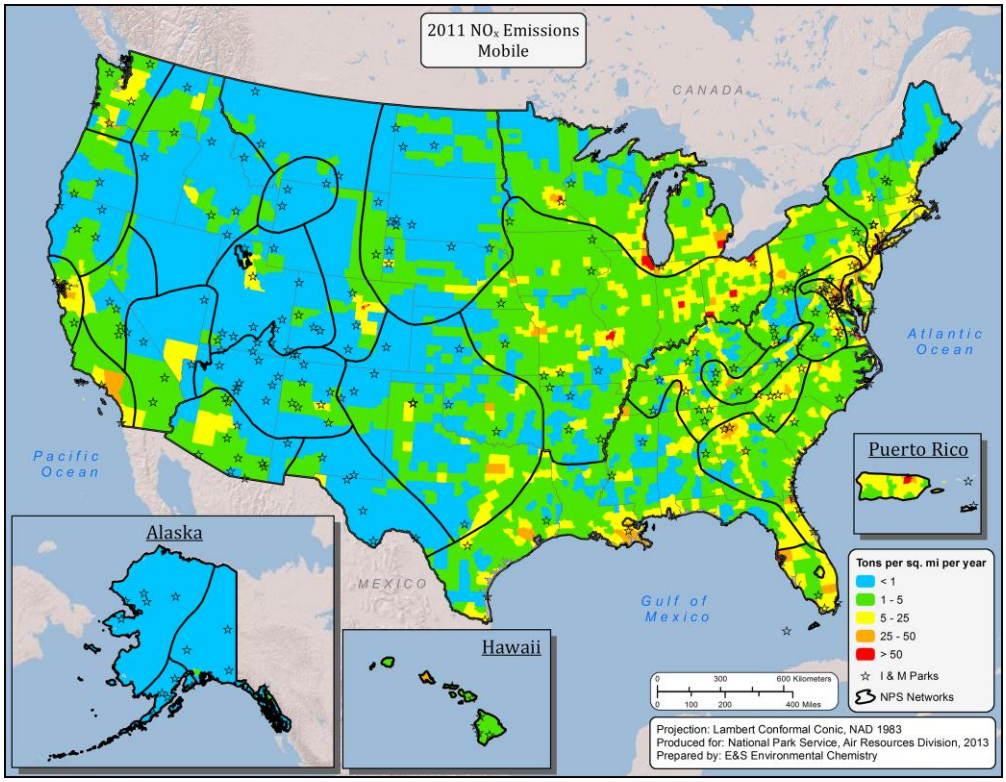


Map A-4. Total SO_2 emissions, by county, attributable to the mobile sector, for the years a) 2002 and b) 2011, based on data from the NEI.

a)

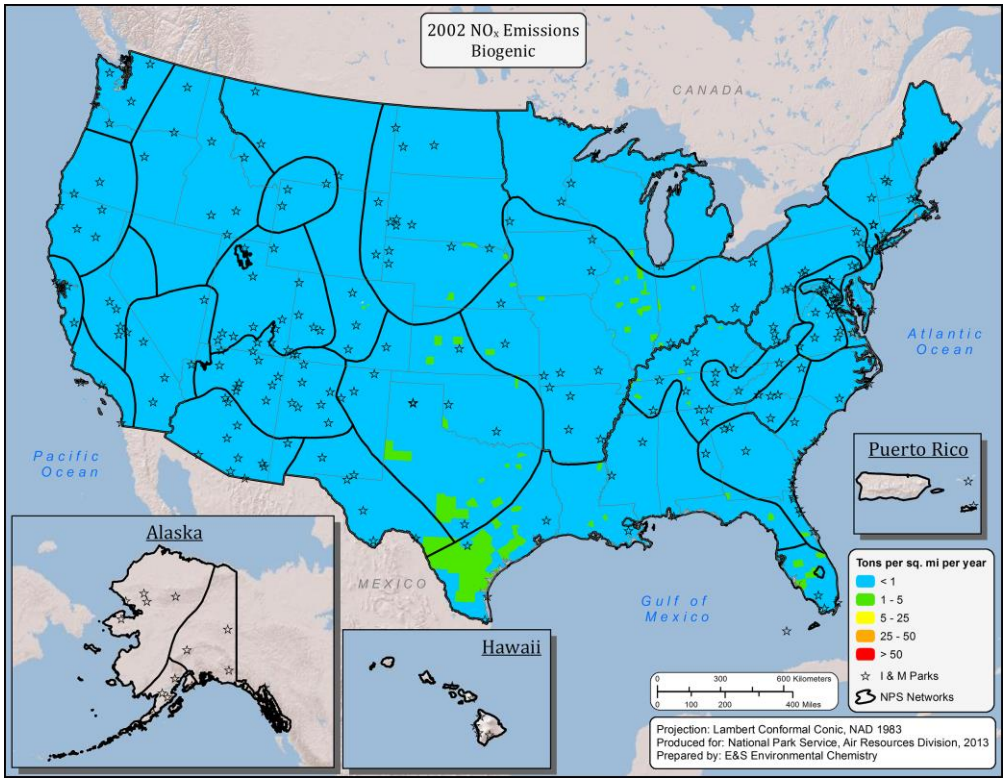


b)

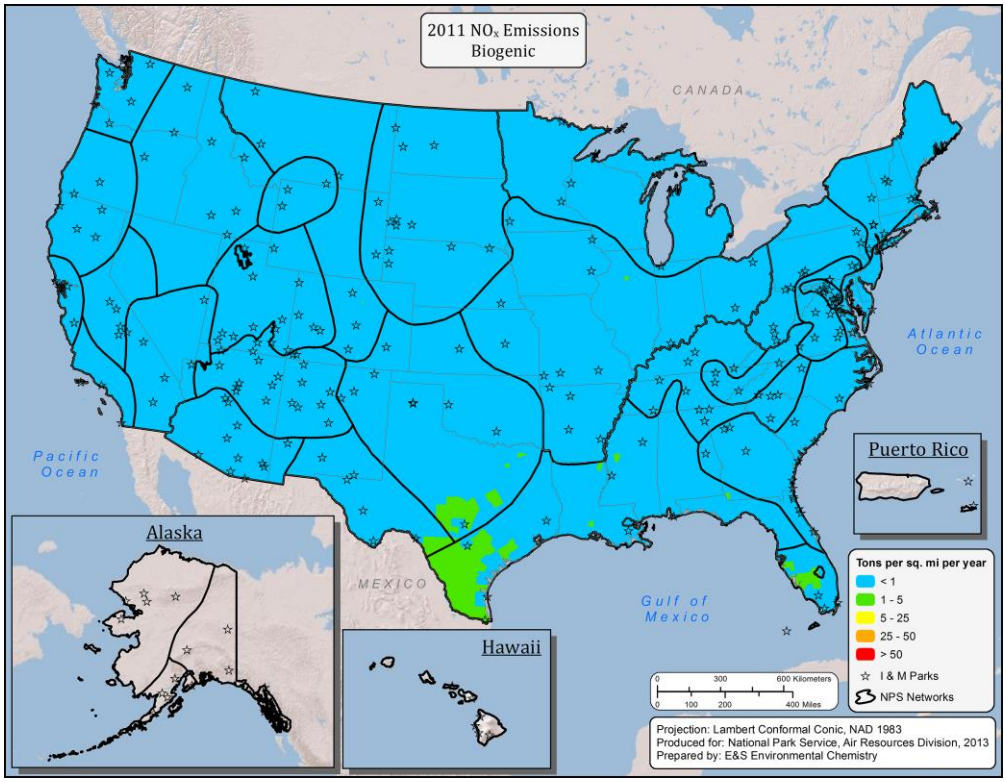


Map A-5. Total NO_x emissions, by county, attributable to the mobile sector for the years a) 2002 and b) 2011, based on data from the NEI.

a)

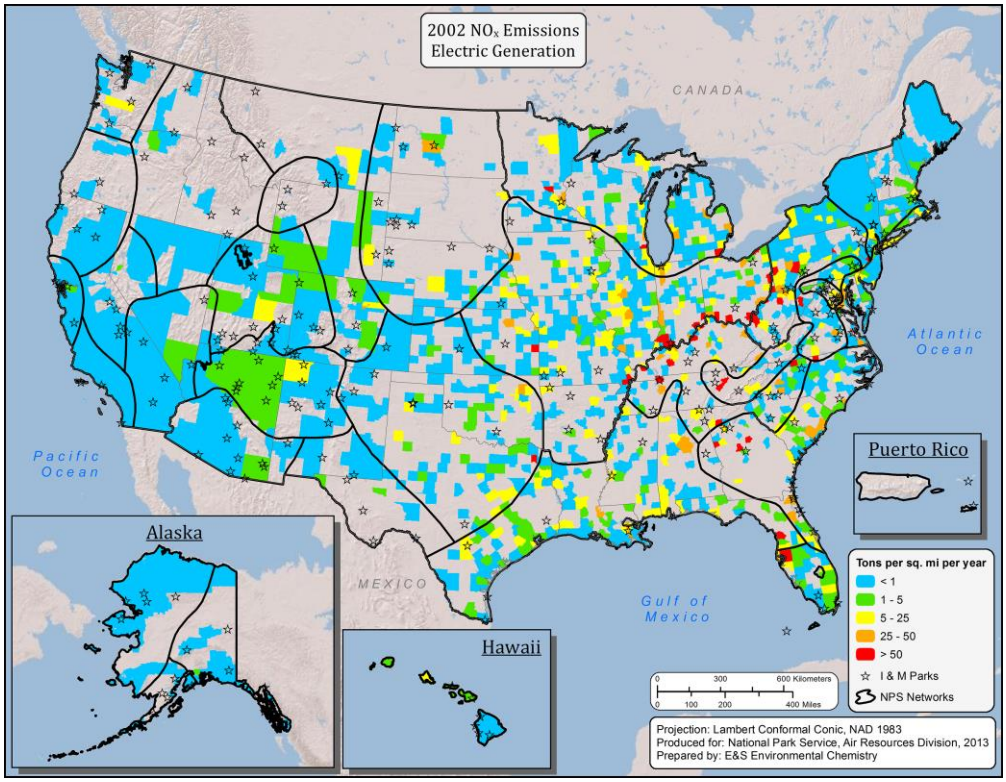


b)

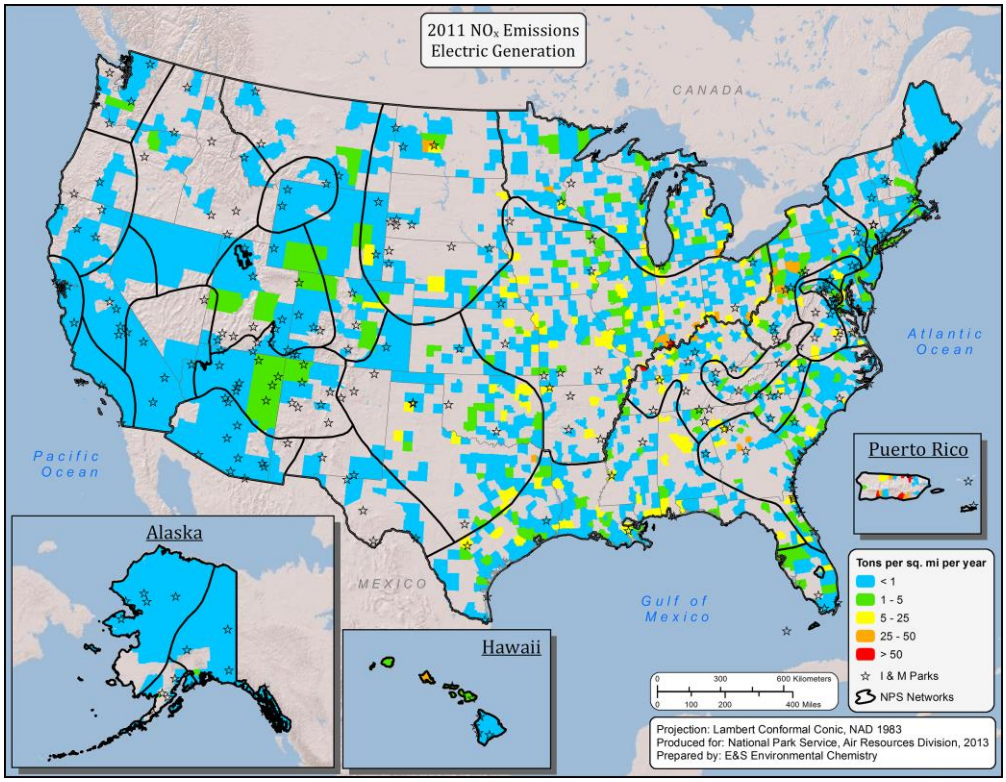


Map A-6. Total NO_x emissions, by county, attributable to biogenics for the years a) 2002 and b) 2011, based on data from the NEI.

a)

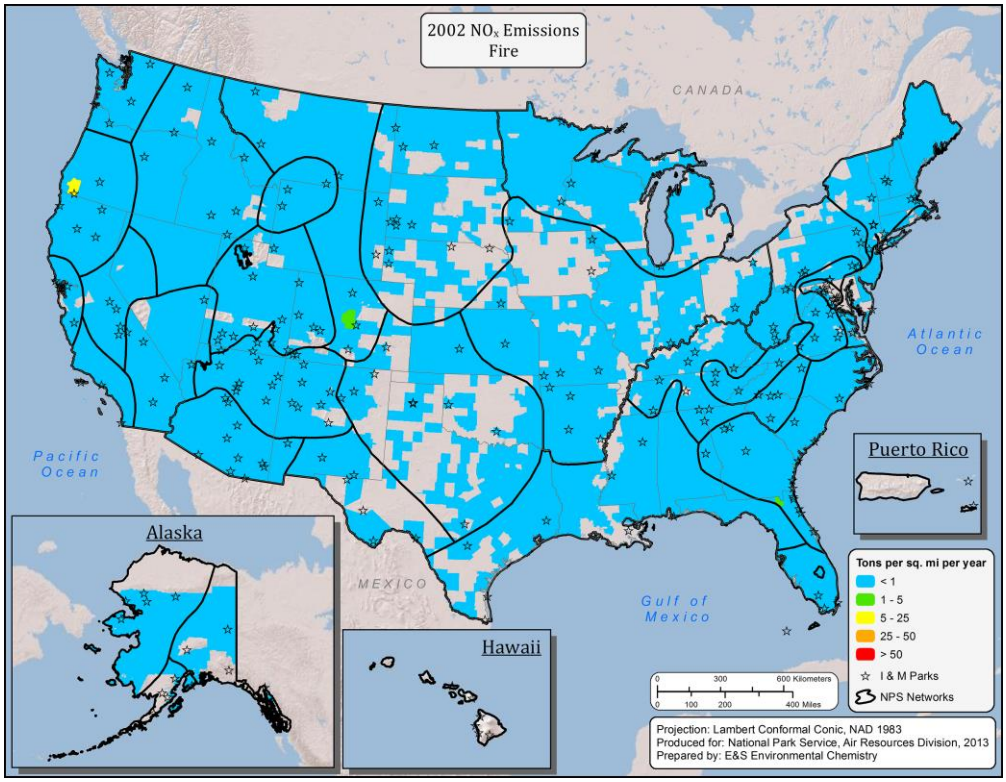


b)

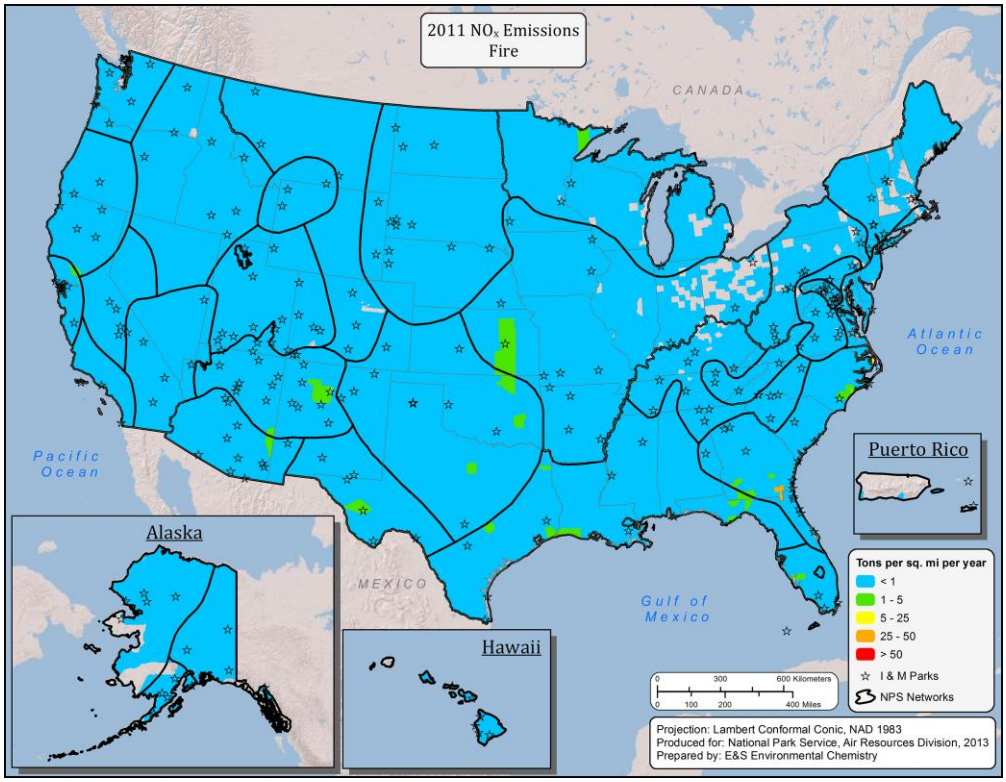


Map A-7. Total NO_x emissions, by county, attributable to the electricity generation sector for the years a) 2002 and b) 2011, based on data from the NEI.

a)

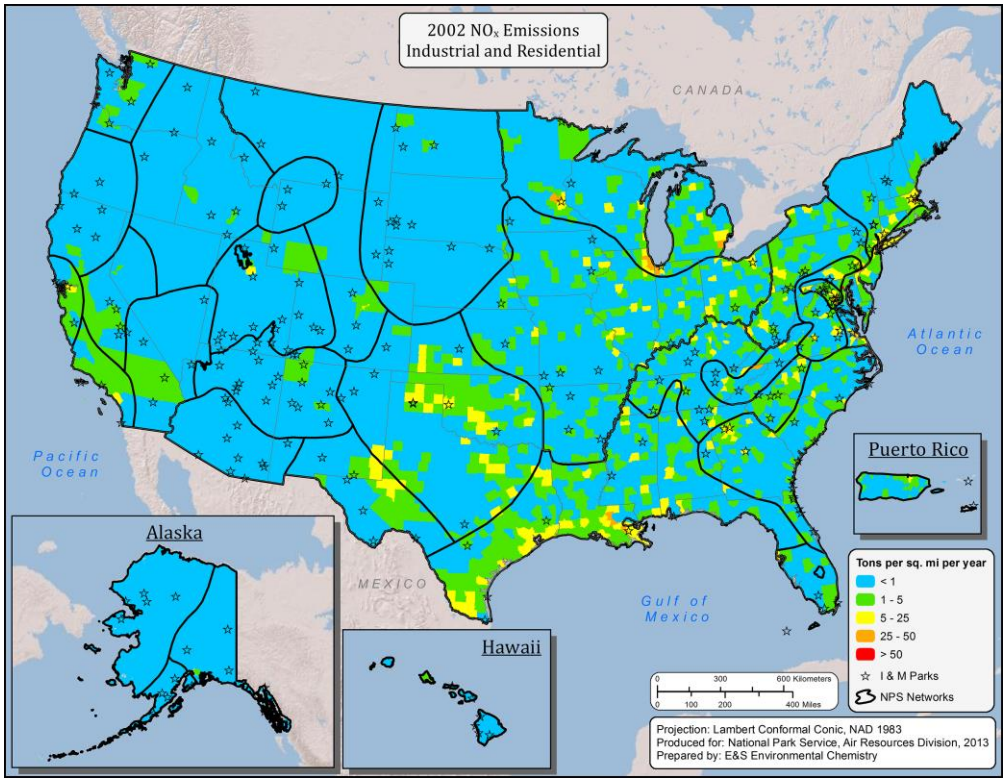


b)

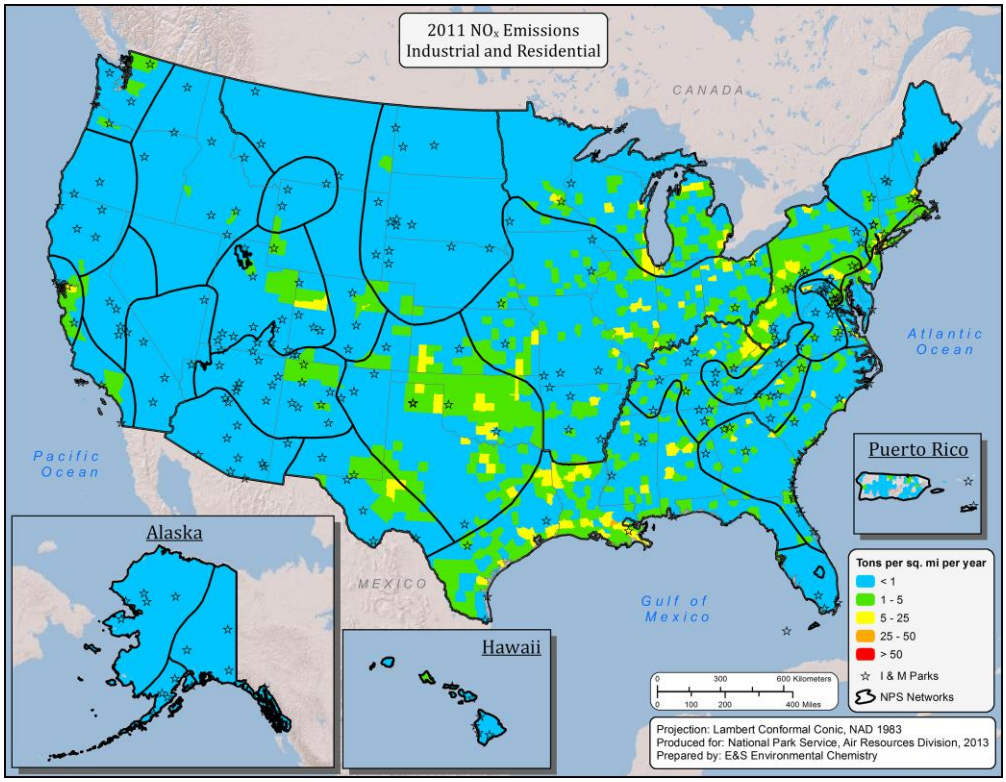


Map A-8. Total NO_x emissions, by county, attributable to fire for the years a) 2002 and b) 2011, based on data from the NEI.

a)

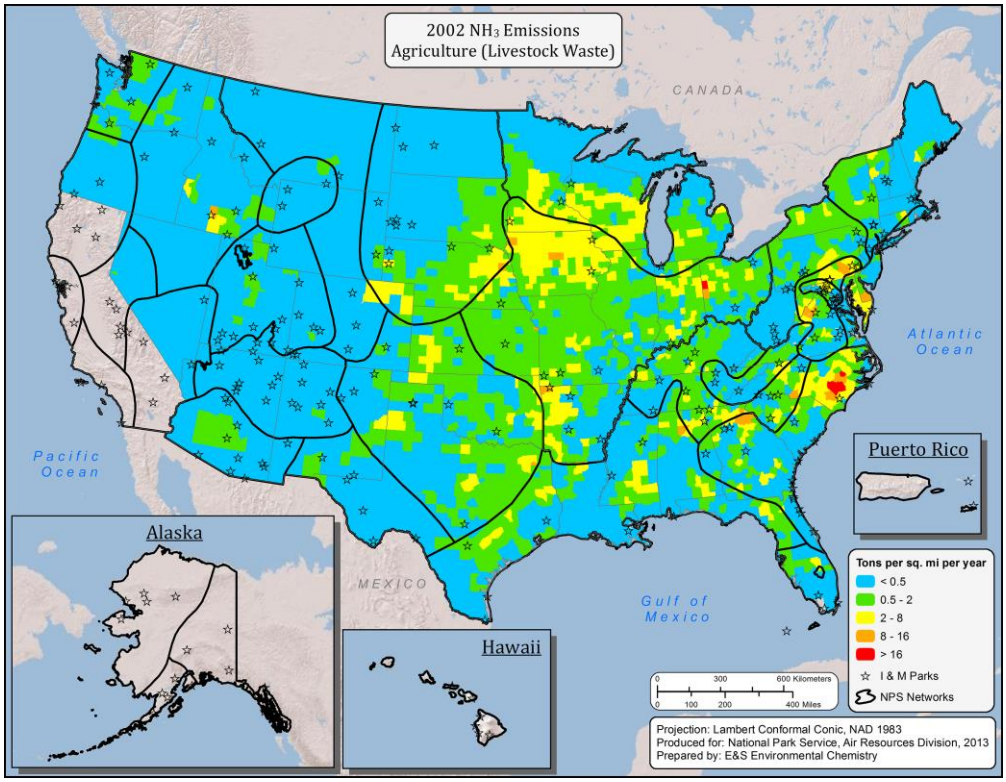


b)

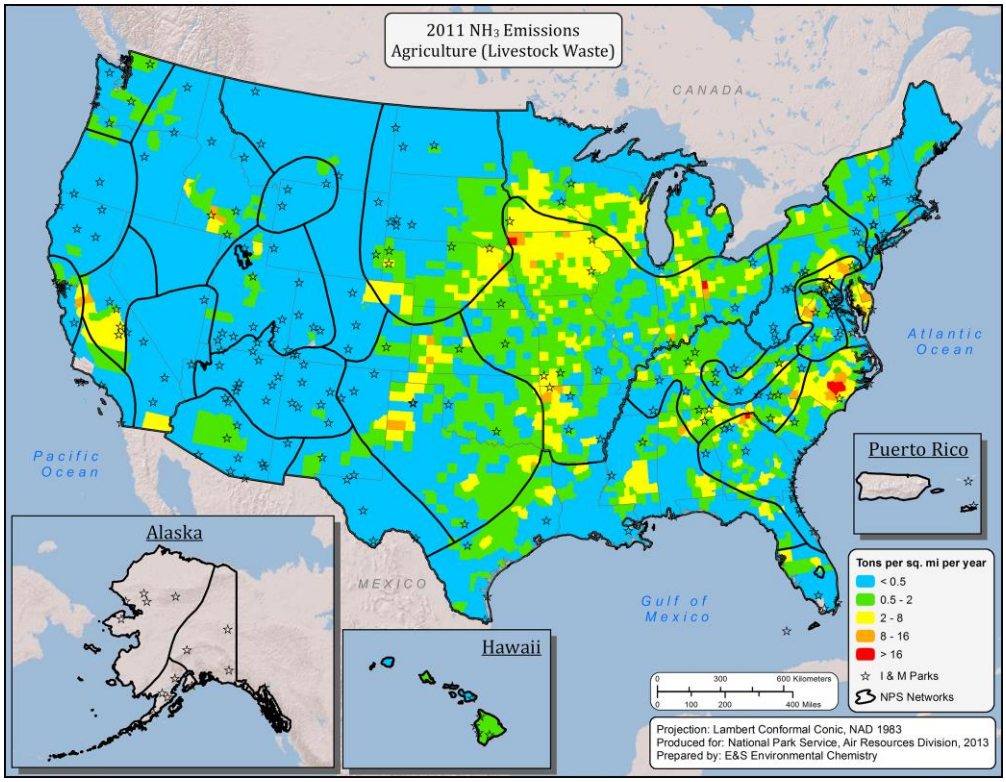


Map A-9. Total NO_x emissions, by county, attributable to the industrial and residential sector for the years a) 2002 and b) 2011, based on data from the NEI.

a)

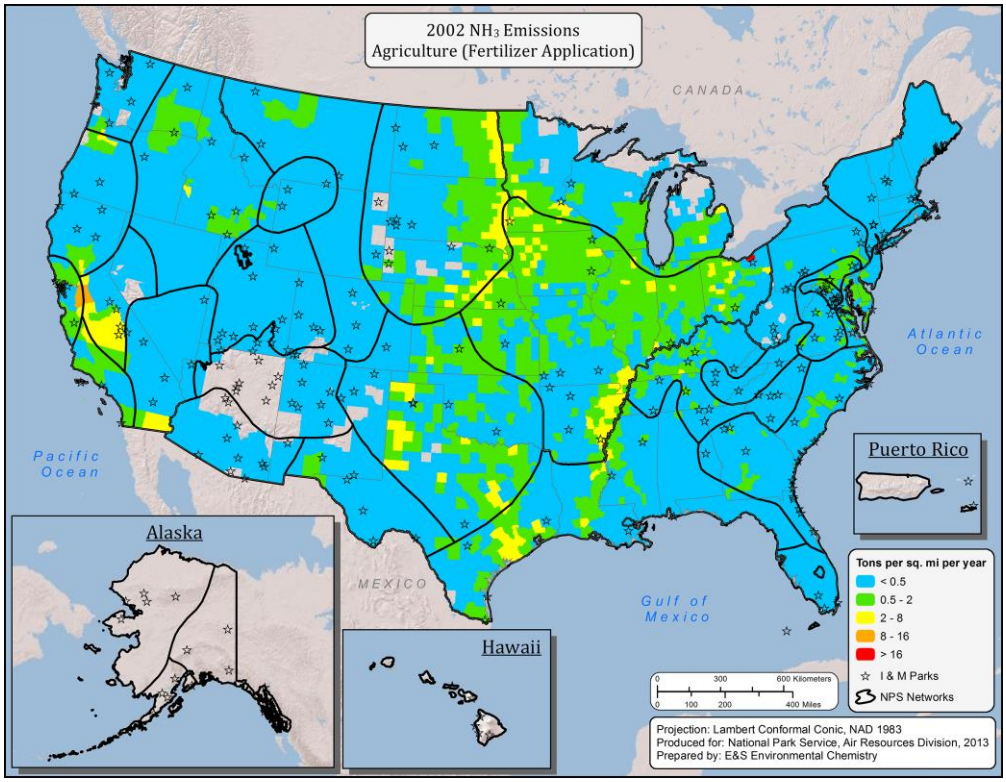


b)

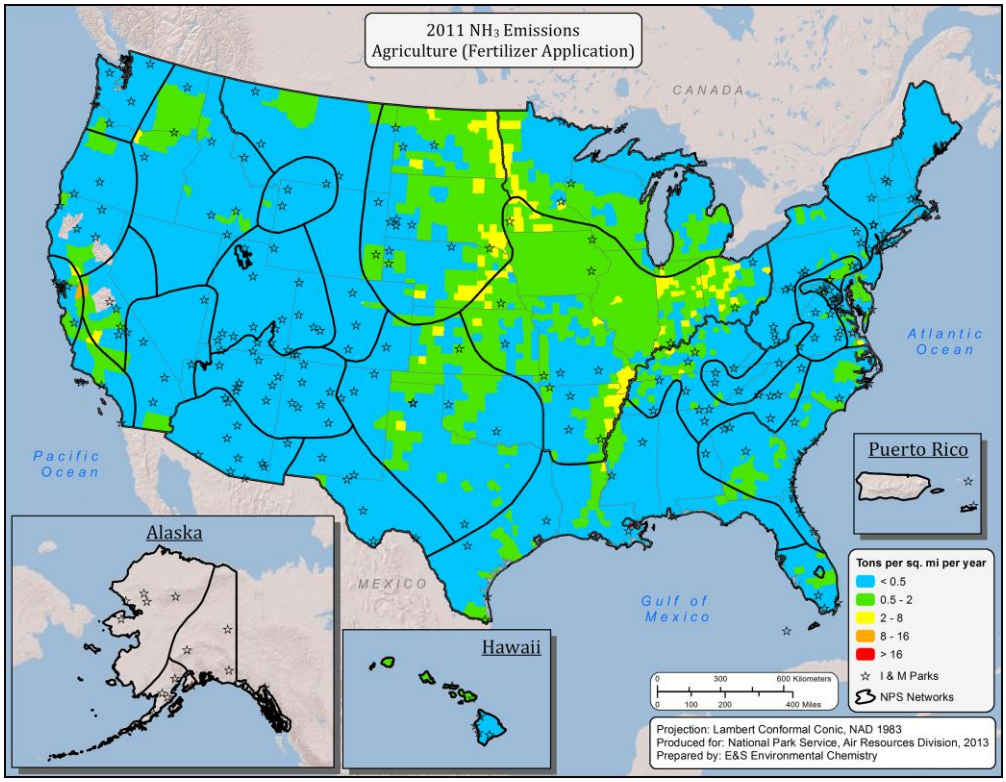


Map A-10. Total NH_3 emissions, by county, attributable to agriculture (livestock waste) for the years a) 2002 and b) 2011, based on data from the NEI.

a)

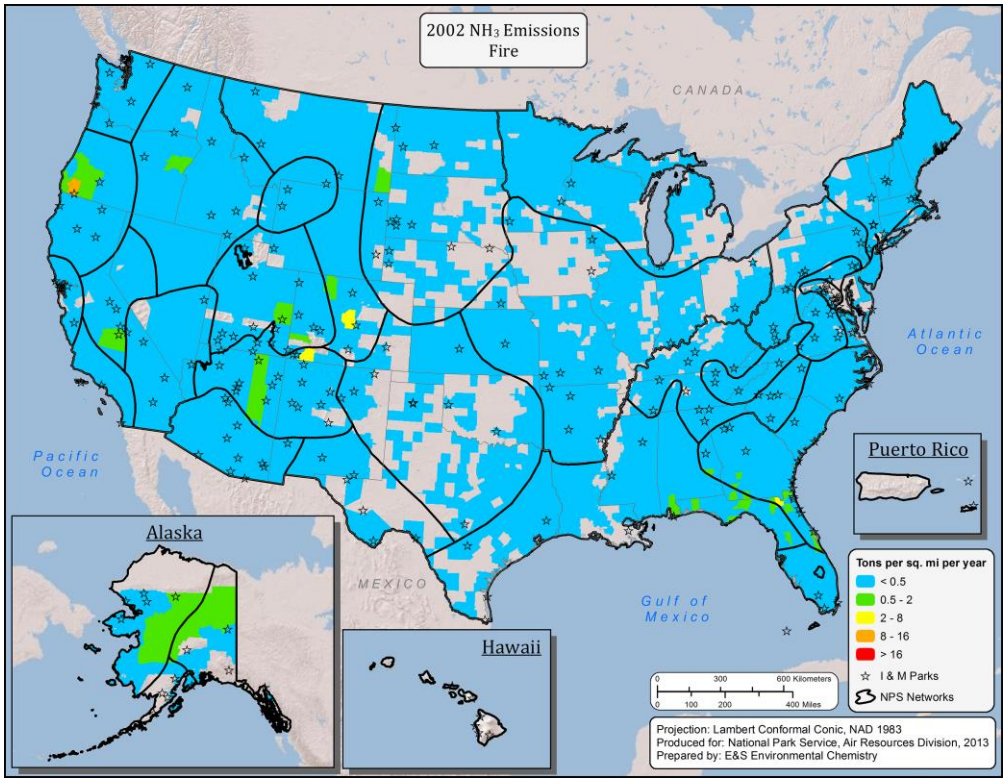


b)

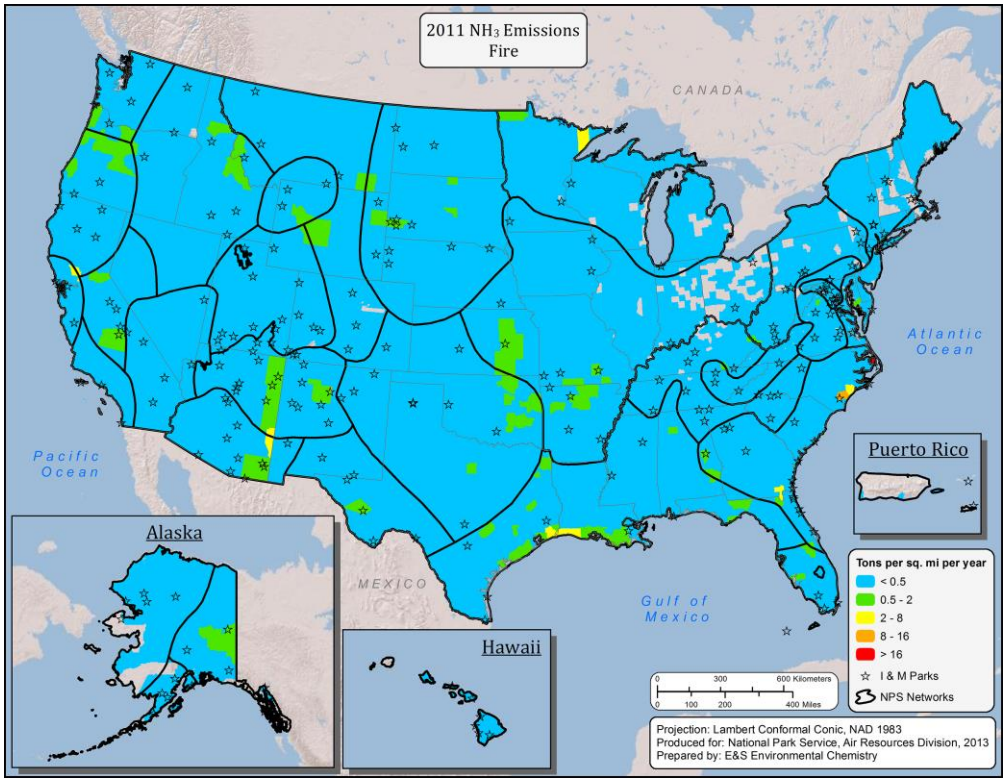


Map A-11. Total NH_3 emissions, by county, attributable to agriculture (fertilizer application) for the years a) 2002 and b) 2011, based on data from the NEI.

a)

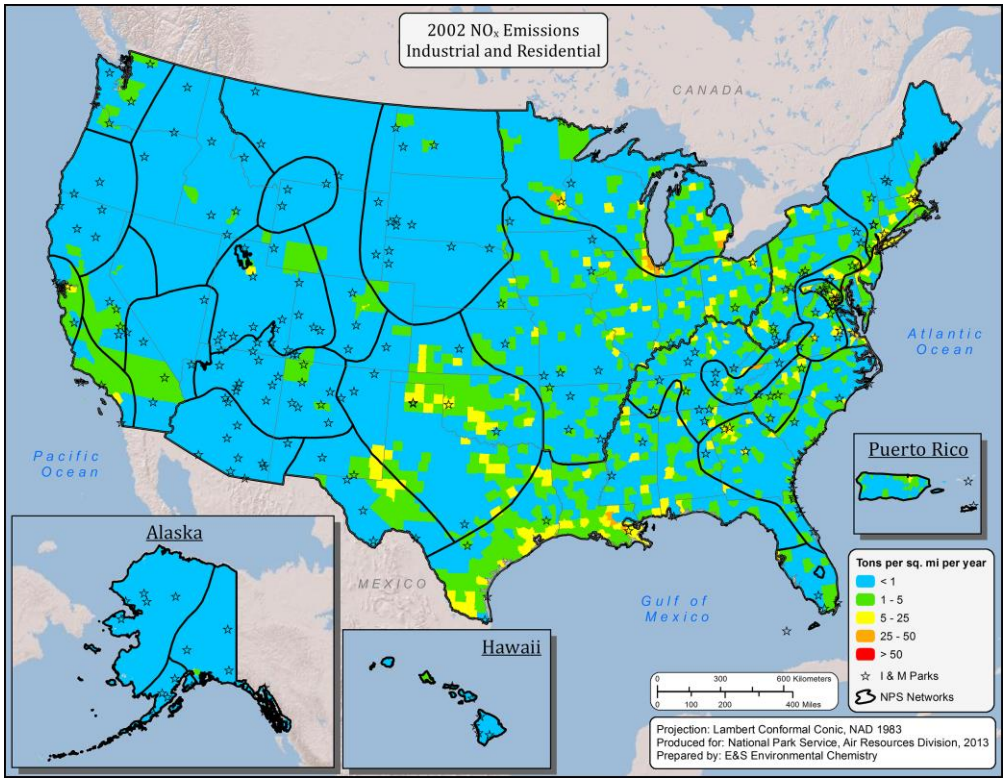


b)

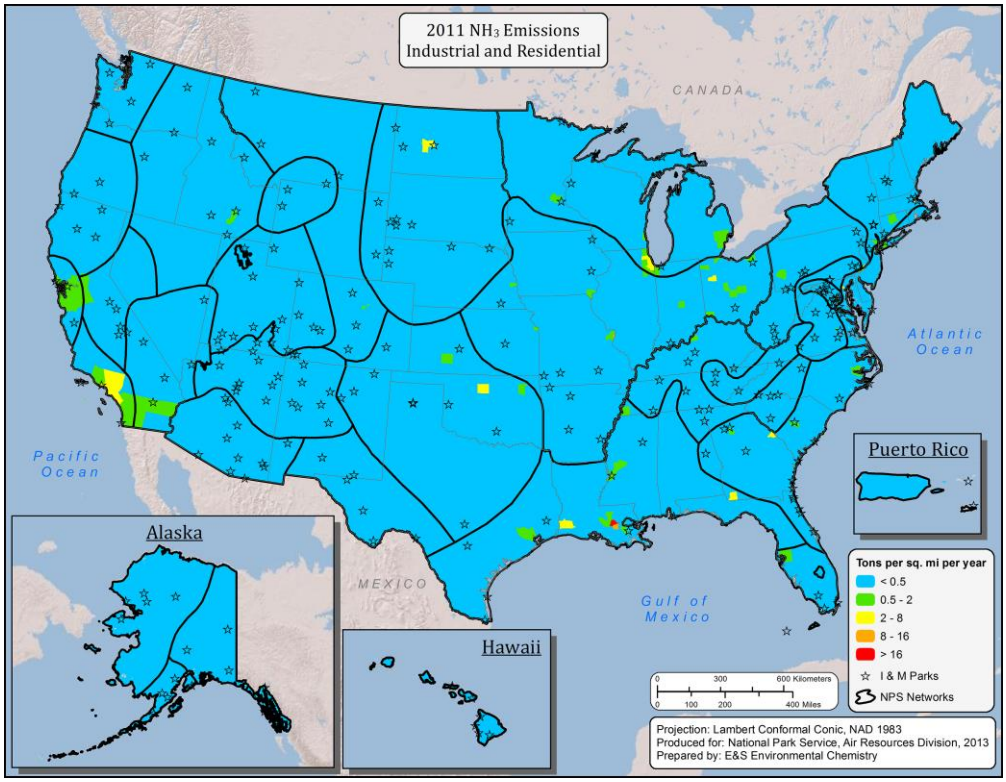


Map A-12. Total NH_3 emissions, by county, attributable to fire for the years a) 2002 and b) 2011, based on data from the NEI.

a)

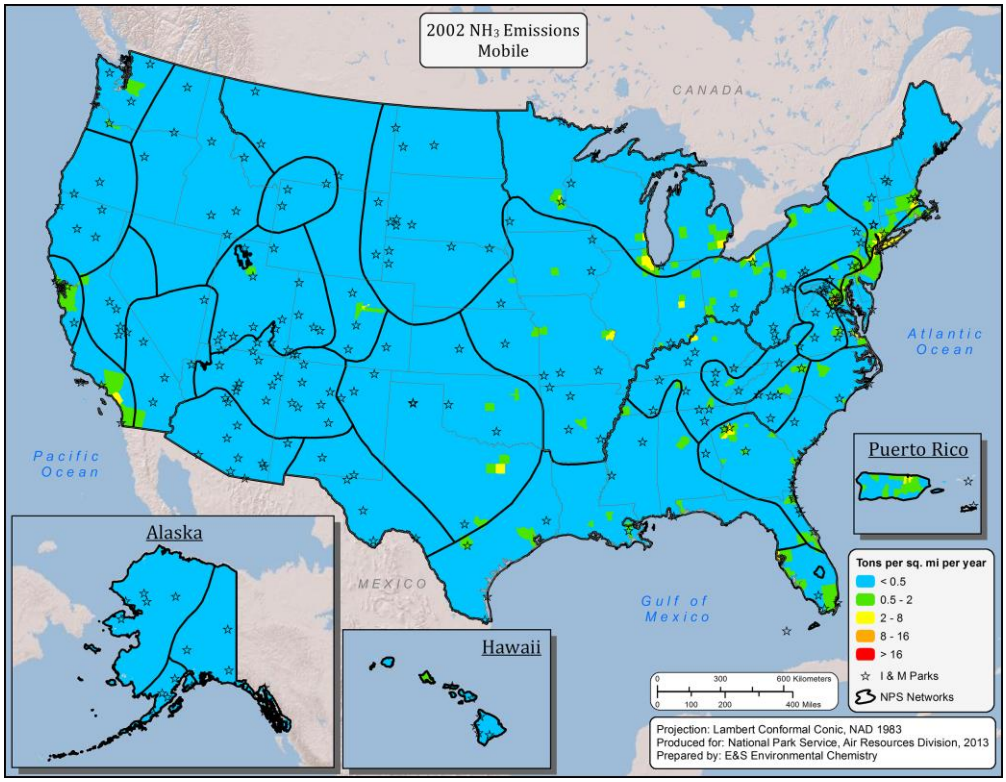


b)

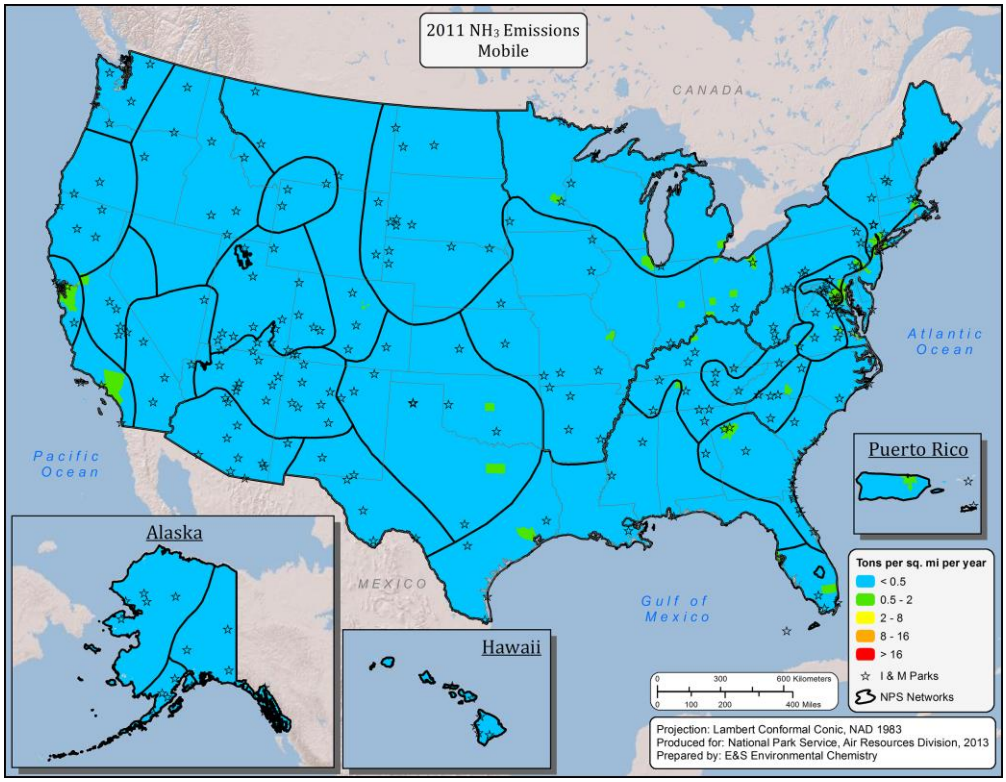


Map A-13. Total NH_3 emissions, by county, attributable to the industrial and residential sector for the years a) 2002 and b) 2011, based on data from the NEI.

a)



b)



Map A-14. Total NH_3 emissions, by county, attributable to the mobile sector for the years a) 2002 and b) 2011, based on data from the NEI.

The Department of the Interior protects and manages the nation's natural resources and cultural heritage; provides scientific and other information about those resources; and honors its special responsibilities to American Indians, Alaska Natives, and affiliated Island Communities.

NPS 999/132252, April 2016

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