SEVEN

Atmospheric Chemistry

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Introduction

In this chapter we discuss air pollution effects on mixed conifer forests and other ecosystems in California with a major focus on the most ecologically influential pollutants, OZONE (O_3) and various nitrogen (N) compounds. From the perspective of human health effects, we focus on fine PARTICULATE MATTER ($PM_{2.5}$) and ozone. We discuss other pollutants briefly in the context of potential toxic effects or impacts on climatic changes. Air quality issues in California have a long history. In precolonial times, long before the modern-day smog problem emerged in the 1940s (Jacobs and Kelley 2008), air quality was almost certainly poor at times due to emissions from lightning-caused fires and those set by Native Americans (Minnich 2008). The Spanish explorer Juan Rodriguez Cabrillo, after sailing into what is now San Pedro Harbor in 1542, named it La Bahia de las Fumas (the bay of smokes) after the darkened skies caused by fires set by Native Americans (Jacobs and Kelly 2008). Approximately 1.8 million hectares burned annually in precontact California, equivalent to 88% of the land area burned in the entire U.S. during extreme wildfire years (Stephens et al. 2007). As a result, skies were likely smoky during much of the summer and fall in that era.

On modern-day air pollution in California, Char Miller (Pomona College, Claremont, California) shared the following personal retrospective: "The postcard on my desk is almost forty years old. Angelenos of a certain age will recognize it—a wide-angled, aerial shot of the downtown core of Los Angeles and its then, much-more modest skyline. Framed by the intersection of the Santa Monica and Harbor freeways, the whole scene is muffled in a brown smear of smog. Barely visible in the deep background, just poking above the thick toxic stew, is a snow-capped Mt. Baldy, the tallest of the San Gabriels. Reads the arch caption: 'Greetings from Los Angeles.' I first spotted the card in the fall of 1972 when I came to Southern California to attend Pitzer College, and immediately sent a steady stream of them to family and friends back east. They got its black humor, which I reinforced when I confessed (and perhaps bragged) that my dorm room was within five miles of Mt. Baldy yet I almost never saw its bold face. Now I see it every day, often with stunning clarity, as if the entire range was etched out of a blue true dream of sky" (Miller 2011).

Summer 1943 marked the beginning of smog in Los Angeles, or at least of public awareness of the approaching air pol-

lution tidal wave. On July 26, 1943, the fourth and by far the most severe smog episode reported that month abruptly appeared in Los Angeles as a thick, suffocating, and noxious haze (City Hunting 1943). Something corrosive was in the air—women's nylon stockings repeatedly developed runs and holes (Jacobs and Kelley 2008), and tire manufacturers noticed that rubber disintegrated faster in Los Angeles than anywhere in the country (SCAQMD 1997). In 1944 plant pathologists at the University of California–Riverside first observed unusual symptoms on agricultural crops in the Los Angeles Basin, which they attributed to a new kind of air pollution: Los Angeles smog (Middleton et al. 1950). It wasn't until the early 1950s that a group led by Ariel Haagen-Smit, a Dutch biochemist at Cal Tech (California Institute of Technology in Pasadena), identified the atmospheric compounds and photochemical reactions responsible for this new kind of air pollution (Finlayson-Pitts and Pitts 2000, Haagen-Smit and Fox 1954).

Since the mid-1940s, air quality in California, especially in its southern part, has been among the worst in the nation. We now know that the infamous Los Angeles PHOTOCHEMICAL smog is a result of uncontrolled emissions of VOLATILE ORGANIC COMPOUNDS (VOCs), carbon monoxide (CO), and NITROGEN OXIDES (NO_x) from millions of motor vehicles and other pollution sources. These compounds undergo photochemical reactions under conditions of high temperatures, light intensity, and THERMAL INVERSIONS typical in summer in the Los Angeles Basin, bounded by several mountain ranges. Thousands of secondary chemical compounds are formed during such reactions, including highly toxic ozone, NITRIC ACID VAPOR (HNO_3), peroxyacetyl nitrate (PAN), and many other compounds toxic to vegetation and humans (Seinfeld and Pandis 1998, Finlayson-Pitts and Pitts 2000).

Unusual symptoms of decline in ponderosa pine (*Pinus ponderosa*) trees were first observed in 1953 in the western portions of the San Bernardino Mountains east of the Los Angeles Basin (Asher 1956). Since the cause of the symptoms was initially unknown, the observed phenomenon was described as "X-disease" by local foresters (Parmeter et al. 1962, Richards et al. 1968, Ohmart 1980, Little 1992). James Asher, a timber management assistant on the San Bernardino National Forest, described his observations of the tree decline in his historic report: "The foliage deterioration, affecting an increasing percentage of the ponderosa pine forest stands within the Arrowhead Ranger District, has been noted with growing concern. This effect, known as the 'X Disease' or 'Needle Dieback' is causing loss of vigor and thus a lessening of annual increments on an alarming number of trees. Though the causative agent is classed as 'unknown,' mortality is occurring." The report suggested possible causes of the malady, but in Asher's view the decline was due to "a heavy concentration of air pollutants borne onto the foliage of the ponderosa pine" (Asher 1956, Little 1992). Subsequent groundbreaking studies conducted by Paul Miller, a U.S. Forest Service scientist, with the use of controlled fumigation of seedlings and branches of mature trees, later showed that ozone was responsible for so-called X-disease, or chlorotic decline (Miller et al. 1963). Symptoms on native ponderosa and Jeffrey pines (*Pinus jeffreyii*) in the San Bernardino Mountains were eventually found to include CHLOROTIC MOTTLE, premature needle loss, reduction of terminal and diameter growth, deterioration of root systems, greater susceptibility to bark beetles, and eventual death of trees (Grulke et al. 2009, Miller 1992).

Since smog became an undeniable problem in the Los Angeles Basin in the 1940s, it has taken decades of struggle on the local, state, and national levels to build the political capital and legislative clout needed to pass emissions control regulations that have made possible major improvements in the air quality of California (Jacobs and Kelly 2008). Various science-based air pollution regulations have been introduced by the California Air Resources Board and local Air Quality Management Districts (http://www.arb.ca.gov/html/brochure/history.htm). As a result of these regulations and their enforcement, air pollution in the Los Angeles Basin has been improving since the 1970s. Air pollution regulation initiated in California strongly influenced the passage of the CLEAN AIR ACT and the development of national standards for controlling major toxic air pollutants (http://www.epa.gov/air/caa/) (Table 7.1).

Temporal and Spatial Patterns of Air Quality: An Overview

While naturally produced air pollution is important (e.g., volcanic emissions of sulfurous gases and AEROSOLS, ozone and nitric acid vapor produced by lightning, emissions of methane (CH_4) from bogs and marshes, dust released from deserts and other arid areas), presently air pollution caused by various anthropogenic activities have much larger effects on human and ecosystem health (Finlayson-Pitts and Pitts 2000, Chapin et al. 2011). Anthropogenic air pollution has been affecting terrestrial ecosystems in California for many decades. In the past, high concentrations of sulfur dioxide (SO_2) or hydrogen fluoride (HF) emitted from point sources such as power plants or metal smelters had only local negative effects on vegetation. Rapid urbanization, increase of automobile traffic, and expansion of various anthropogenic activities (industry, agriculture, residential emissions, and many small business enterprises) made poor air quality a major problem in the Los Angeles Basin and other areas, especially the Central Valley and the San Francisco Bay Area. Agricultural emissions significantly contribute to severe air pollution problems in the Central Valley and in portions of the eastern Los Angeles Basin with high density of dairy farms (Carle 2006). Changes in landscape use, such as the massive movement of dairy farms from the Los Angeles Basin into the Central Valley in the 2000s, have significantly changed the spatial distribution of agricultural emissions in the state (Farrell 2005).

In the seventy years since the first episodes of severe smog in the Los Angeles Basin occurred, air quality in California has generally improved (Pollack et al. 2013). This has resulted from active, science-based implementation of strict air pollution measures, such as the introduction of catalytic converters, reformulation of gasoline, reduced consumption of gasoline in cars and other vehicles, and elimination of most heavy-emitting stationary and mobile pollution sources. These trends are reflected more broadly in a continuing decrease in emissions of nitrogen oxides and reactive organic gases (ROG) in California (Figure 7.1).

However, emissions of fine particulate matter (<2.5 µm in diameter, $PM_{2.5}$) and coarse particulate matter (<10 µm in diameter, PM_{10}) have not decreased or even slightly increased.

Photo on previous page: Air masses contaminated by San Joaquin Valley photochemical smog affect air quality in Sequoia National Park, August 2014. Photo: A. Bytnerowicz.

TABLE 7.1
Air pollutants exhibiting significant effects on California terrestrial ecosystems

Pollutant	Typical concentration ranges in remote areas	Mode of action	Sensitive receptor	Ecological response	References
Ozone (O_3)	1 hour: 0–150 ppb; summer average: 20–80 ppb	Oxygen free radical damage to chloroplasts	Ponderosa and Jeffrey pines	Foliar damage, growth decrease, and increased sensitivity to drought and bark beetle attacks	Bytnerowicz and Grulke 1992, Bytnerowicz et al. 2008
Ammonia (NH_3)	0.2–18.5 µg/m^3 (summer average)	Direct toxicity to oligotrophic lichens; contribution to N deposition	Oligotrophic lichens; native forbs	Changes in lichen communities; increased invasion of grasses (for effects of N deposition, see Table 7.2)	Bytnerowicz and Fenn 1996, Bytnerowicz et al. 2007, Fenn et al. 2011
Nitrogen oxides (NOx)	NO: < 25 ppb NO_2: < 50 ppb	Contribution to N deposition and ozone formation	Various natural vegetation communities	As above	Bytnerowicz et al. 1998
Nitric acid vapor (HNO_3)	0.3–17.5 µg/m^3 (summer average)	Direct toxicity to plant cuticles; contribution to N deposition	Various natural vegetation communities	As above	Bytnerowicz and Fenn 1996, Bytnerowicz et al. 2007
Semivolatile organic compounds (SOCs)	Differ for various compounds	Movement in food chain; accumulation of toxic compounds in animal tissue	Sensitive wildlife species, including pollinators, fish, and mammals	Effects increase with higher position in a food chain	Landers et al. 2010

Many areas in California, especially in its southern part and in the Central Valley, suffer from poor air quality and frequent violations of air pollution standards for ozone and particulate matter. In January 2014 extremely high fine particulate matter levels, exceeding by about three times the national air quality standard of 35 mg m^{-3}, were recorded near Fresno and Bakersfield in the Central Valley. Such levels are caused by high pollution emissions, lack of rain that typically cleans the air, stagnant conditions, and prolonged thermal inversions that keep polluted air masses near the ground. Concentrations of fine particulates and other pollutants are largely driven by weather conditions (pers. comm., Dr. Barbara Finlayson-Pitts, University of California–Irvine). Chemical reactions that convert nitrogen oxides and other gases from cars, diesel trucks, trains, ships, and factory emissions into haze-forming fine particles are further accelerated by greater humidity when fog blankets the area (Barboza 2014). Five of ten of the most polluted U.S. urban areas (Bakersfield; Los Angeles–Long Beach–Riverside; Visalia-Porterville; Hanford-Corcoran; and Fresno-Madera) are in California (American Lung Association 2013). Emissions from these pollution source areas influence air quality in remote areas of California, with pronounced ecological effects. For example, the San Bernardino Mountains and the Sierra Nevada Mountains are strongly affected by air pollution from, respectively, the Los Angeles Basin and the Central Valley (Figure 7.2).

Elevated levels of ambient ozone and atmospheric NITROGEN DEPOSITION, though much lower than several decades

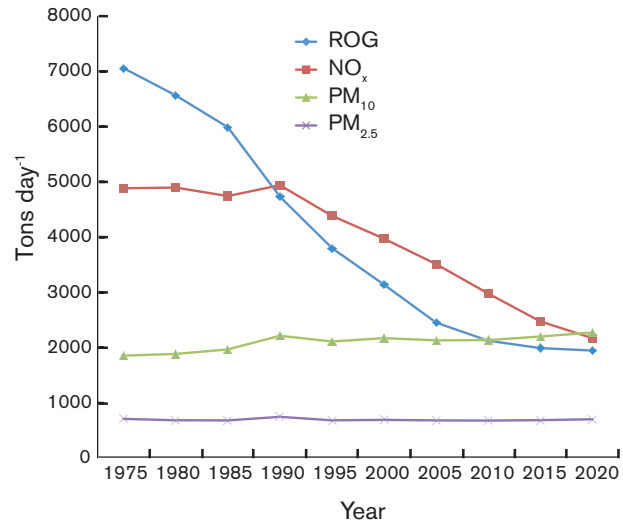

FIGURE 7.1 Changes in air pollution emissions in California: totals for reactive organic gases (ROG), nitrogen oxides (NOx), particulate matter <2.5 µm in diameter ($PM_{2.5}$) and particulate matter <10 µm in diameter (PM_{10}). Source: California Air Resources Board. http://www.arb.ca.gov/aqd/almanac/almanac.htm. Accessed June 10, 2015.

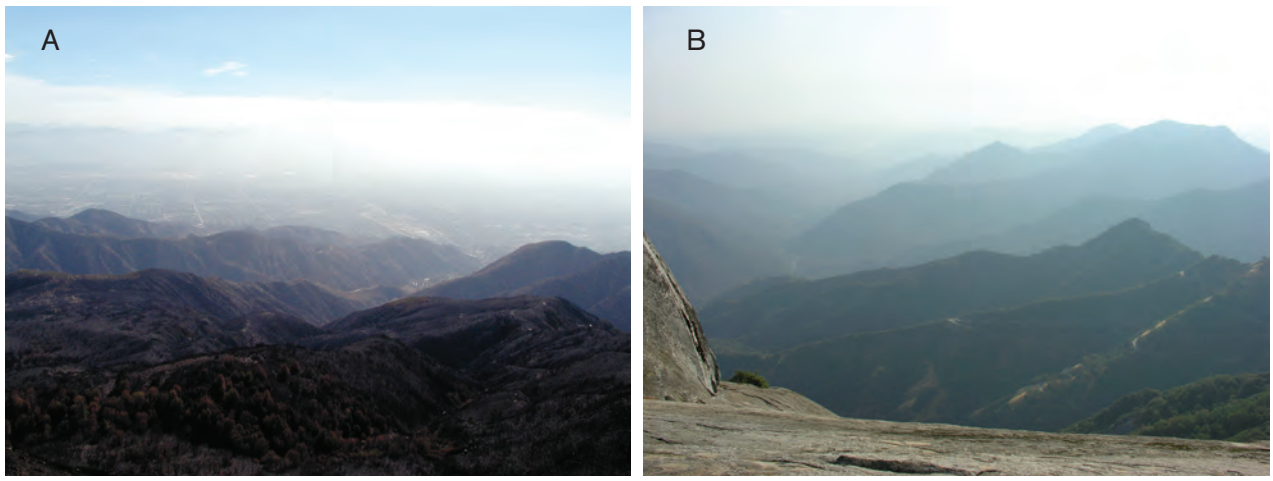

FIGURE 7.2 Photochemical smog.

A Over the Los Angeles Basin, view from the San Bernardino Mountains, June 2003. Photo: Andrzej Bytnerowicz.

B Over the San Joaquin Valley, view from Moro Rock, September 2014. Photo: Andrzej Bytnerowicz.

ago, still pose severe threats to vegetation in California. Long-range transport of polluted air masses from Mexico (Wang et al. 2009) or across the Pacific from Asia also contribute substantially to elevated ozone levels (Vingarzan 2004). Increased ozone concentrations could also result from climate change in California. Prolonged lack of precipitation and stagnant conditions resulted in serious smog problems in downtown Los Angeles and its coastal areas in January 2014 (Barboza 2014). Other potentially toxic pollutants, such as PESTICIDES from extensive agricultural operations or deposition of mercury (Hg) from combustion processes, can be transported long-distance and deposited to sensitive ecosystems in remote areas of California. The long-term biogeochemical effects of these pollutants on aquatic and terrestrial ecosystems are of concern.

Statewide Atmospheric Circulation Patterns and Their Implications for Air Pollution Transport

Pollutant transport is a complex phenomenon. Sometimes transport can be straightforward, as when wind blows from one area to another at ground level and carries polluted air masses with it. However, most often transport patterns are three-dimensional and can take place either at the surface or high above the ground (aloft). Winds can blow in different directions at various heights above the ground. To further complicate matters, winds can shift during the day, moving polluted air masses in multiple directions. Therefore accurate determinations of the impacts of pollution transported from a source area to a downwind area require complex analyses and modeling (Austin et al. 2001).

Air masses in California broadly tend to move from the coast inland. Typical summer wind patterns for California (Figure 7.3) involve northwesterly winds, which are a consequence of GEOSTROPHIC BALANCE between the subtropical ANTICYCLONE over the eastern Pacific Ocean and thermal low pressure over the California, Nevada, and Arizona deserts driving air masses onshore to the coastal ranges (Fujioka et al. 1999). In the San Francisco Bay area, at the gap of the coastal ranges, these onshore winds diverge into two streams: one flowing northward into the Sacramento Valley and the other southward into the San Joaquin Valley. The marine layer (or marine air mass trapped by thermal inversion) over the California coast usually dissipates in the Central Valley due to ADIABATIC HEATING and mixing with warm air aloft. Warm, boundary layer air masses overlaying the Central Valley are stratified by a weak thermal inversion at 1,000 to 1,300 meters. Daytime land heating generates local ANABATIC WINDS from the southwest and west along the western Sierra Nevada slopes, moving polluted air masses eastward into the Sierra crest. Finally, marine air funnels through low passes in the Sierra Nevada into the Mojave Desert and the Modoc Plateau (Minnich and Padgett 2003). In the upper half of the state, the fall and spring wind patterns are quite similar to those in summer, although generally much weaker. However, during winter the combination of strong horizontal mixing aloft in the presence of the jet stream, weak INSOLATION, and strong thermal inversions overlaying the Central Valley shifts wind patterns and reduces transport of polluted air masses into the Sierra Nevada (Hayes et al. 1992, Minnich and Padgett 2003).

In southern California during warm summers, cool winds flow inland from the Pacific Ocean (Figure 7.4). These winds mostly consist of the "onshore south" and "sea breeze" types, which constitute approximately 70% of all summer winds (Hayes et al. 1992). Pacific high pressure affects air pollution transport in the South Coast Air Basin primarily through a SUBSIDENCE INVERSION, which caps the mixing layer and promotes cloud-free conditions above the inversion. In the resulting absence of clouds, temperatures rise faster over land than over the ocean. This causes a sea breeze from the Pacific Ocean moving eastward and inland. Cloudless skies above the inversion also make more sun available for photochemical reactions inside the inversion layer, resulting in formation of high concentrations of ozone and other secondary air pollutants. Since the sea breeze is typically capped at relatively low elevation (~1,000 meters above sea level), the polluted air masses are trapped inside the Los Angeles Basin (Fujioka et al. 1999). With air moving eastward in the late afternoon hours, the western slopes of the San Bernardino and San Gabriel Mountains experience very high ozone concentrations (Bytnerowicz et al. 2008). The Transverse and Peninsular mountain ranges form barriers to the movement of sea breezes further inland. While spring wind patterns are quite similar to those in summer, fall and especially winter patterns are quite different. They involve

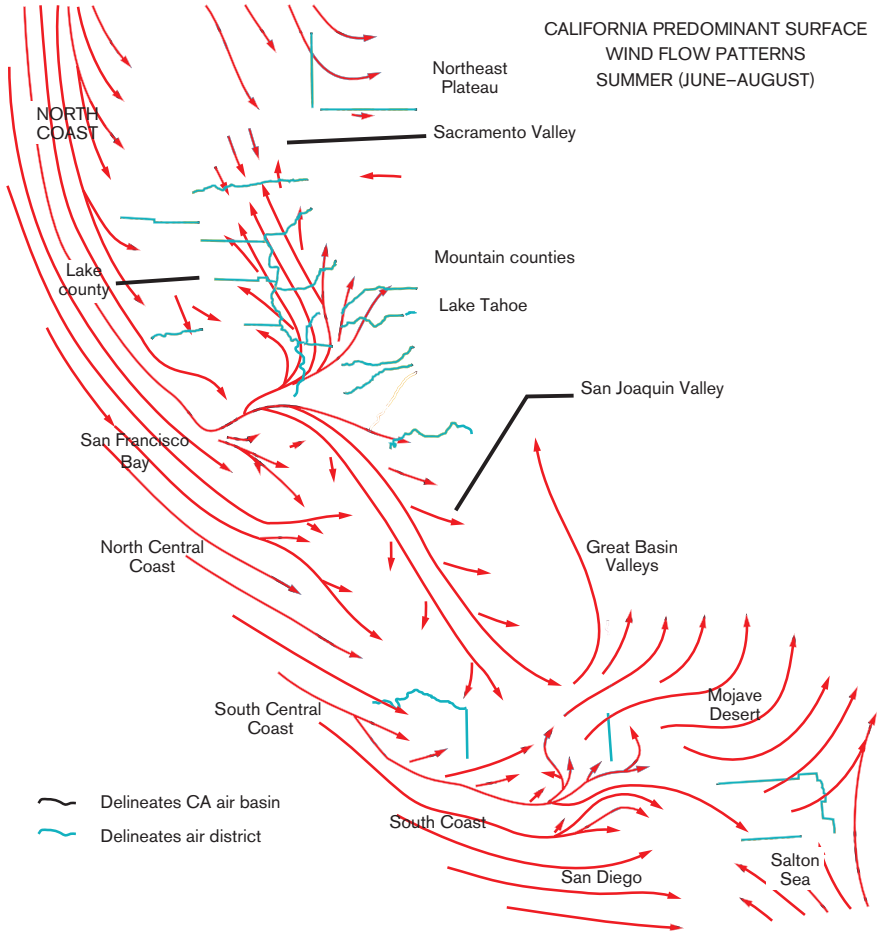

FIGURE 7.3 Typical summer (June–August) wind flow patterns in California. Green shaded areas are forests on federal lands. Source: Hayes et al. 1992.

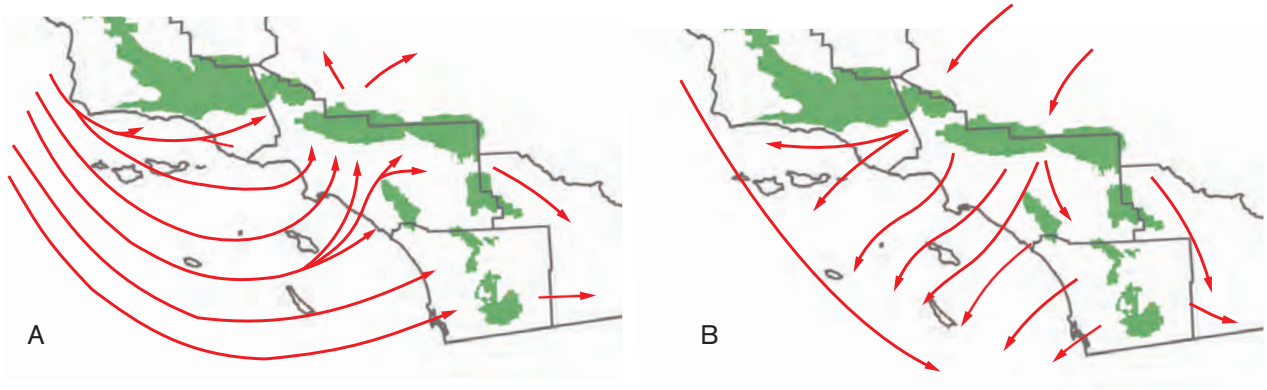

FIGURE 7.4 Examples of wind patterns in the South Coast Air Basin. Green shaded areas are forests on federal lands. Source: Hayes et. al. 1992.

A Summer, onshore south.

B Winter, full Santa Ana winds.

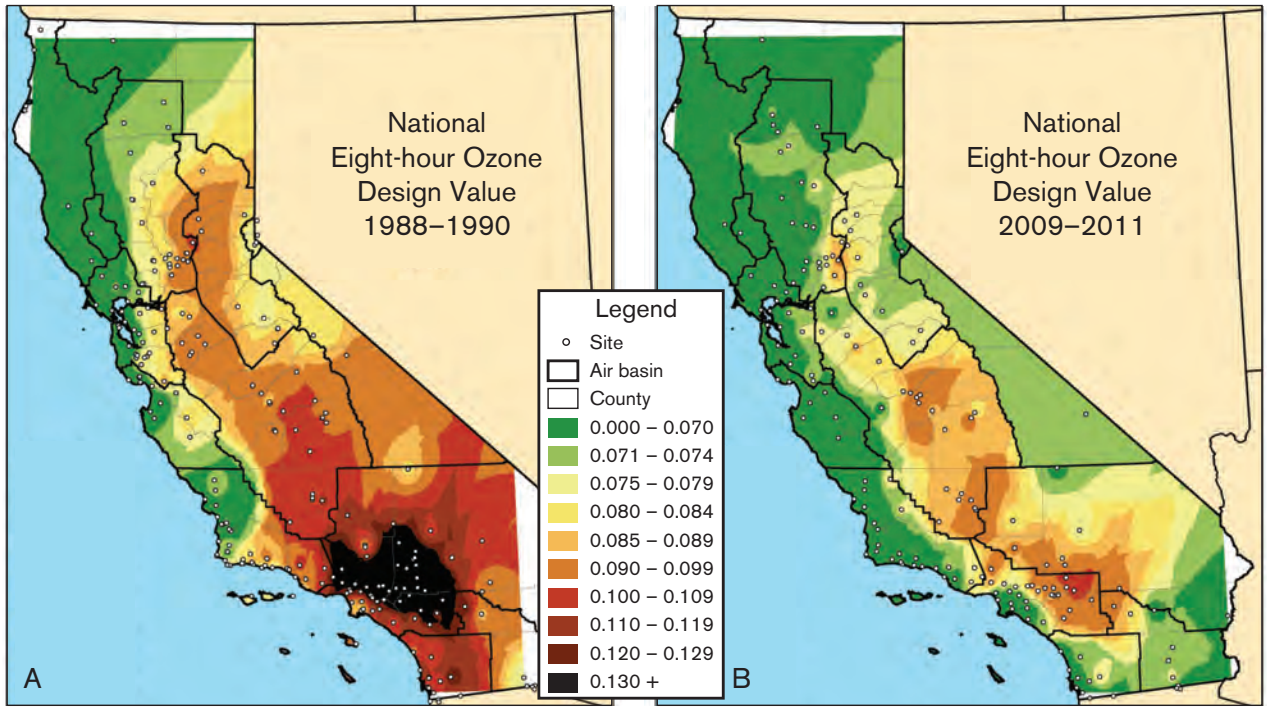

FIGURE 7.5 Three-year average of fourth-highest daily maximum eight-hour average ozone concentrations (ppm, parts per million) for (A) 1988–1990 and (B) 2009–2011. Values >0.075 ppm indicate exceedance of the federal primary air pollution standard. Source: California Air Resources Board.

much higher occurrence of the southerly, downslope/transitional, and strong SANTA ANA WINDS (Hayes et al. 1992), which sweep the air from the Los Angeles Basin into the Pacific Ocean (see Figure 7.4) (see also Chapter 2, "Climate").

Ozone Distribution in Space and Time

California still has the highest ozone air pollution and associated highest risks to human health in the U.S. (CASTNET 2013). However, recent progress in ozone air quality in California is impressive (Figure 7.5), and further improvement in O_3 air quality is expected. Part of this improvement mirrors broader geographic trends. Many Northern Hemisphere sites that showed increasing ozone concentrations fifteen to thirty years ago also show slightly decreasing or flattening patterns in the past ten to fifteen years (Oltmans et al. 2013). In California's urban areas maximum hourly ozone concentrations declined drastically between the 1970s and mid-1990s and have continued to shrink since, but at a more moderate rate (Pollack et al. 2013). The most improved ozone air quality took place in the South Coast Air Quality Management District (AQMD) followed by the San Diego AQMD. The Sacramento, San Francisco, and San Joaquin AQMDs had much smaller decreases in ozone concentrations (Figure 7.6). Similar to urban area trends, significant improvement of ozone air quality has also been observed in remote areas in California, including the San Bernardino Mountains (Bytnerowicz et al. 2008, Bytnerowicz, Fenn et al. 2013).

Projections based on recent data (approximately fifteen years of data) at the highly polluted San Bernardino Mountains site of Crestline indicate that by 2100, ozone levels could become similar to those before the photochemical smog episodes started occurring in the Los Angeles Basin in the 1940s (Bytnerowicz, Fenn, et al. 2013). These long-term projections have very large uncertainty because of many factors—especially demographic, economic, and technological—that will affect future air pollution emissions, levels, and spatial distribution. From an ecological perspective, information on ozone distribution in remote forested areas is essential. Because the reliability of pollution transport models in complex mountain terrain is limited (Austin et al. 2001), the USDA Forest Service has developed methods for ground-level air pollution monitoring in remote California areas using PASSIVE SAMPLERS. Samplers provide long-term average (weeks, months) concentrations of various air pollutants, and their results are spatially displayed as geostatistically generated maps (Arbaugh and Bytnerowicz 2003, Frączek et al. 2003, Panek et al. 2013). Because evaluations of the phytotoxic potential of ozone also requires information on its real-time concentrations, portable battery and solar-panel operated UV-absorption O_3 monitors are also used (Bognar and Birks 1996).

Results of 1999 air pollution monitoring conducted over the entire range of the Sierra Nevada Mountains show the highest summer ozone averages in its southern portion (Frączek et al. 2003). High levels of the pollutant are caused by LONG-RANGE TRANSPORT of polluted air masses containing ozone and its precursors (nitrogen oxides, volatile organic compounds, carbon monoxide) from the California Central Valley (on the southwestern Sierra slopes) and southern California (on the southeastern Sierra slopes). Further north, ozone concentrations are generally lower, although the mid-elevation western slopes, including Sequoia and Kings Canyon and Yosemite National Parks, may experience very high levels at times (Bytnerowicz et al. 2002, Burley and Ray 2007). Ozone can penetrate into the eastern portions of the Sierra Nevada along canyons and valleys crossing the range, as shown by high concentrations sustained along the southwest-northeast tran-

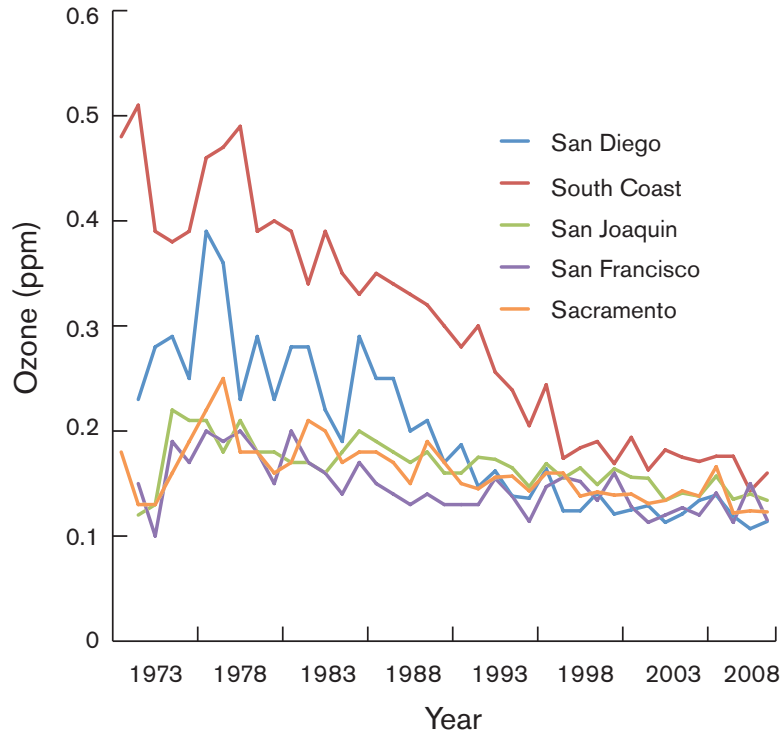

FIGURE 7.6 Changes in maximum one-hour ozone concentrations (ppm, parts per million) in selected Air Quality Management Districts in California. http://www.arb.ca.gov/aqd/almanac/almanac.htm. Accessed June 10, 2015.

sect of the San Joaquin River drainage (Cisneros et al. 2010). However, high mountain ranges can also create barriers to the movement of the polluted air masses (Frączek et al. 2003). For example, polluted air masses from the California Central Valley are blocked from entering the Lake Tahoe Basin by the high elevation massif of the Desolation Wilderness (Gertler et al. 2006). Ozone air pollution in the Lake Tahoe Basin is thus generally low and mainly results from local ozone generation. Because levels of other pollutants are also low, air quality in the Lake Tahoe Basin is generally good, with high visibility during most of the summer. Occasionally, at some of the most polluted sites on the eastern side of the Lake Tahoe Basin, elevated ozone occurs due to long-range transport of polluted upper layers of tropospheric air (Gertler et al. 2006).

Ozone concentrations decline as air masses move over forested slopes due to stomatal uptake of the pollutant, as was reported in the western portions of Sequoia and Kings Canyon National Park (Bytnerowicz et al. 2002). This is in contrast to only slightly decreasing ozone concentrations when air masses move over a sparsely forested landscape (Cisneros et al. 2010). Generally, the lowest ozone pollution in a remote eastern Sierra Nevada site (Devils Postpile National Monument) occurred when air masses originating from over the Pacific Ocean crossed the California Central Valley at high elevation (3–5 kilometers). The highest ozone pollution at Devils Postpile occurred when air masses swept at low altitudes over the highly polluted San Francisco Bay Area and the San Joaquin Valley (Bytnerowicz, Burley et al. 2013).

Ozone distribution in southern California generally shows strong west-to-east concentration gradients, as seen in the San Bernardino Mountains, with very high concentrations on their western side and low concentrations, close to CONTINENTAL BACKGROUND levels, in their eastern portion near Big Bear Lake (Bytnerowicz et al. 2008). A similar pattern occurs in the most O_3-polluted national park in the U.S., Joshua Tree National Park in the western Mojave Desert (Burley et al. 2014). Finally, southwest-to-northeast winds move polluted air masses from the Los Angeles Basin, causing elevated ozone concentrations in the Owens Valley and southeastern Sierra Nevada Mountains (Figure 7.7).

Biological Effects of Ozone

Ozone effects on vegetation depend on its concentrations, and more specifically on the dose of ozone taken up by plants as well as their physiological and biochemical defense mechanisms. Negative effects of ozone on plants include chlorophyll damage, reduced stomatal conductance, premature foliar senescence, and lower root mass, resulting in decreased photosynthesis (Grulke 2003). Various abiotic and biotic characteristics, especially water availability, ambient temperature, and the presence of pests and diseases, influence the extent of ozone phytotoxic effects (Bytnerowicz and Grulke 1992).

Severe ozone effects of this type on sensitive ponderosa and Jeffrey pines in the San Bernardino Mountains continued through about 1978. Subsequently and through 1988, tree condition improved as ozone concentrations decreased (Miller et al. 1989). Values for several PHYTOTOXIC INDICES calculated for the 1980–2010 period at Crestline, the most highly ozone-polluted site in the San Bernardino Mountains, indicate pronounced decreases during the 1980–1995 period and much slower decreases since 1995. Values at this site still place the western side of the San Bernardino Mountains as the forested area with the highest ozone exposure in the U.S. and with high potential for negative effects (Bytnerowicz et al. 2008, Vollenweider et al. 2013).

Ozone injury in forests of the Sierra Nevada Mountains was

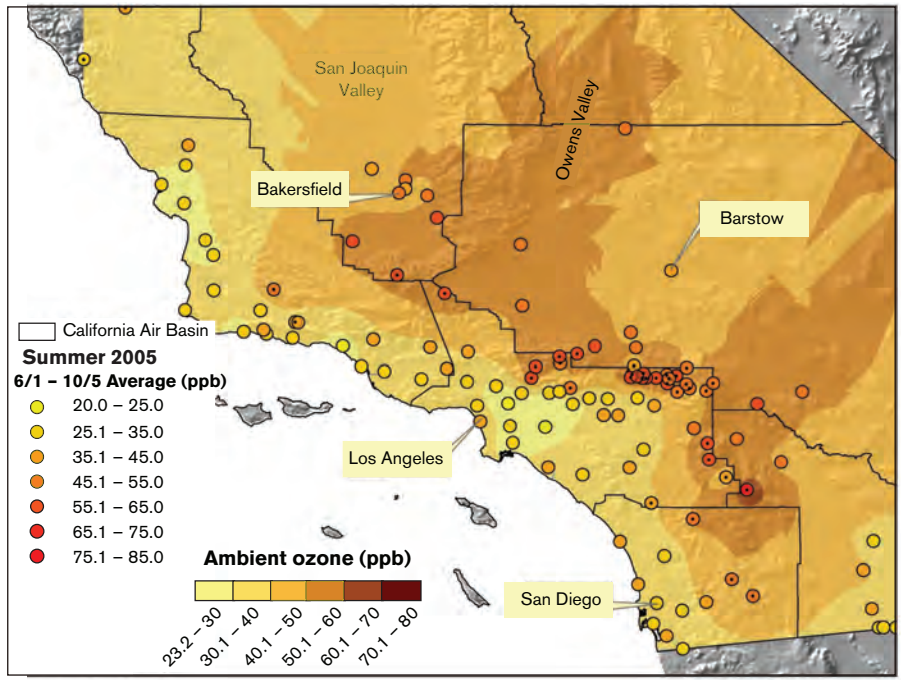

FIGURE 7.7 Influence of southern California smog on ozone air pollution in the Owens Valley and eastern Sierra Nevada, summer 2005 (1ppb = 10^{-3} ppm). Source: A. Bytnerowicz, unpublished.

first observed in the western portions of Sequoia National Forest and Sequoia National Park in the early 1970s (Miller and Millecan 1971, Williams et al. 1977). In the 1970s and 1980s ozone injury symptoms were discovered over most of the Sierra Nevada, with more than 20% of the evaluated ponderosa and Jeffrey pines affected. The lowest ozone injury was detected in the northern Sierra Nevada, while in the southwestern portion of the range the most severe symptoms occurred (with the worst injury at elevations lower than 1,800 meters). Injury declined along the west-to-east direction across the Sierra Nevada as distance from the highly polluted California Central Valley increased (Carroll et al. 2003). The most severe injury of pines was found in Sequoia and Kings Canyon and Yosemite National Parks (respectively 39% and 29% of trees with injury symptoms). Ozone injury evaluations repeated in 2000 on a subset of monitoring plots in the Sierra and Sequoia National Forests showed a gradual increase in the number of trees with chlorotic mottle—from 21% of all trees in 1977 to 40% in 2000. In the southern Sierra Nevada Mountains plots, tree mortality reached 7% during that period. Ozone was the primary cause of tree death (36.5%), with bark beetles and wood borers responsible for 27.9% of mortality, followed by forest fire (15.4%) and other less significant factors such as broken tops, mistletoe, logging damage or windthrow (Carroll et al. 2003). Ozone is a predisposing damaging factor in tree mortality in California, while other factors (such as drought and infestations by various species of bark beetles) are the ultimate cause of mortality (Fenn et al. 2003, Minnich and Padgett 2003).

Nitrogen Air Pollution and Atmospheric Deposition: Forms and Spatial Trends

Contrary to patterns of wet deposition of nitrogen for the U.S., the highest levels of nitrogen deposition in the country, particularly to forested areas, occur in certain areas of California and are caused mainly by dry nitrogen deposition (Fenn et al. 2012). As with other air pollutants, spatial distribution of nitrogen-containing pollutants and resulting nitrogen deposition depend on the location and size of emission sources as well as geographic and climatic characteristics. In California's Mediterranean climate more than 85% of precipitation occurs in winter. In the mountains most of the winter precipitation occurs as snow, except the coastal ranges that receive mostly rainfall (Aschmann 1973). Summer precipitation is scarce and occurs as short-lasting storms. Generally winter precipitation does not contain high concentrations of nitrogenous ions because it mostly brings very clean Pacific moisture and is typically quite evenly distributed throughout the state (Bytnerowicz and Fenn 1996). Because of low concentrations of locally generated gaseous pollutants in winter, SCAVENGING of those compounds does not result in high concentrations of nitrate (NO_3^-) or ammonium (NH_4^+) in precipitation, except within or downwind of major urban or agricultural emissions sources (Fenn and Bytnerowicz 1997). Most of the elevated levels of nitrogen deposition in southern and central California (Figure 7.8) therefore result from high dry summer deposition of various reactive nitrogen species.

An important exception is in regions where fog events occur. Fog water, when coinciding with nitrogen emissions sources, contains ionic concentrations typically one to two orders of magnitude greater than in precipitation (Collett et al. 1990, Fenn et al. 2000). As a result, in many montane regions of California, inputs from fog or cloud water are an important nitrogen deposition pathway (Fenn and Bytnerowicz 1997, Fenn and Poth 2004). As much as one-third of total annual deposition inputs may occur from fog water in forested sites of California with regular fog occurrence (Collett et al. 1989, Fenn et al. 2000, Fenn and Poth 2004).

The dominance of dry deposition is magnified in airsheds with frequent thermal inversions, such as the Los Angeles

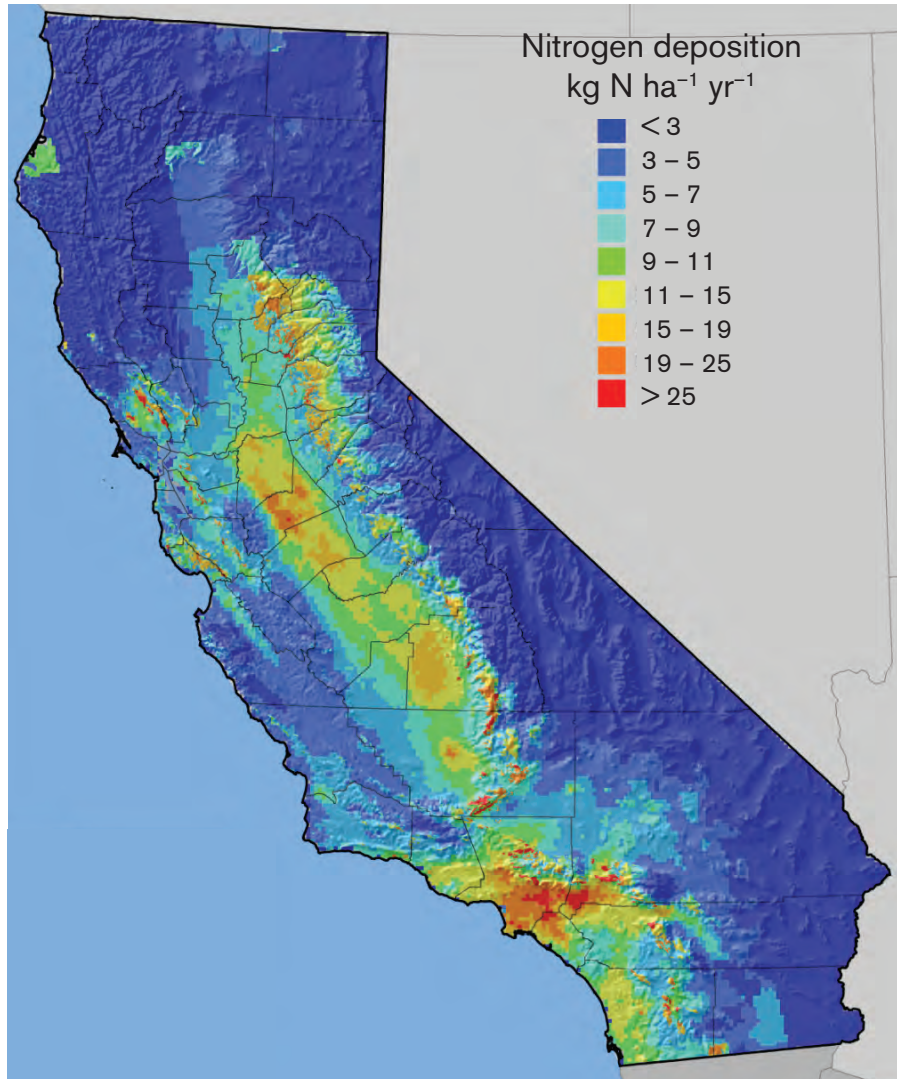

FIGURE 7.8 Map of nitrogen deposition in California. Source: Fenn et al. 2010.

and San Joaquin Valley air basins. In general, nitrogen dry deposition to California ecosystems is dominated by surface deposition of nitric acid vapor and AMMONIA (NH_3), particulate nitrate and ammonium, and stomatal uptake of gaseous nitrogenous pollutants such as nitrogen oxides, ammonia, and nitric acid vapor. The importance of ammonia and nitric acid vapor in California reflects high ambient concentrations of these compounds as well as their high deposition velocities, which result in very high fluxes (Bytnerowicz and Fenn 1996). In addition to inorganic nitrogen deposition involving the compounds discussed earlier, organic reactive nitrogen species can significantly contribute to total nitrogen deposition (Greaver et al. 2012).

The use of passive samplers has allowed us to understand the distribution of major contributors to inorganic nitrogen deposition in southern California (Figure 7.9). In summer 2005 a major monitoring effort showed highly elevated concentrations of ammonia, especially near Riverside and along Interstate 10 leading to Palm Springs and beyond, with concentrations decreasing from west to east. High ammonia concentrations in the Riverside area are most likely caused by agricultural emissions from the nearby, upwind dairy operations in Norco and Chino. However, emissions of ammonia from combustion engines equipped with three-way catalytic converters (Bishop et al. 2010, Kean et al. 2000) also contribute to high concentrations of the pollutant in California. High ammonia concentrations were not observed in the San Bernardino Mountains, probably due to few local emissions sources of this pollutant and to its effective deposition onto various landscape receptors. However, eastern portions of Joshua Tree National Park experienced elevated ammonia concentrations. Highest concentrations of nitrogen dioxide were recorded in the Riverside area, most likely due to its generation from nitric oxide emitted by local traffic and also to long-range transport of the pollutant from upwind Los Angeles. High concentrations of nitrogen dioxide were also observed near Palm Springs, indicating effects of traffic on Interstate 10. Concentrations of nitric acid vapor were also highest in the Riverside and Palm Springs areas. This can be explained by (1) photochemical production of the pollutant from its precursors in the Los Angeles area and along local transportation routes and (2) eastward movement of the polluted air masses with the onshore summer winds. These findings illustrate how passive monitoring networks for measuring concentrations of nitrogen pollutants can greatly increase our understanding of spatial and temporal dynamics of the

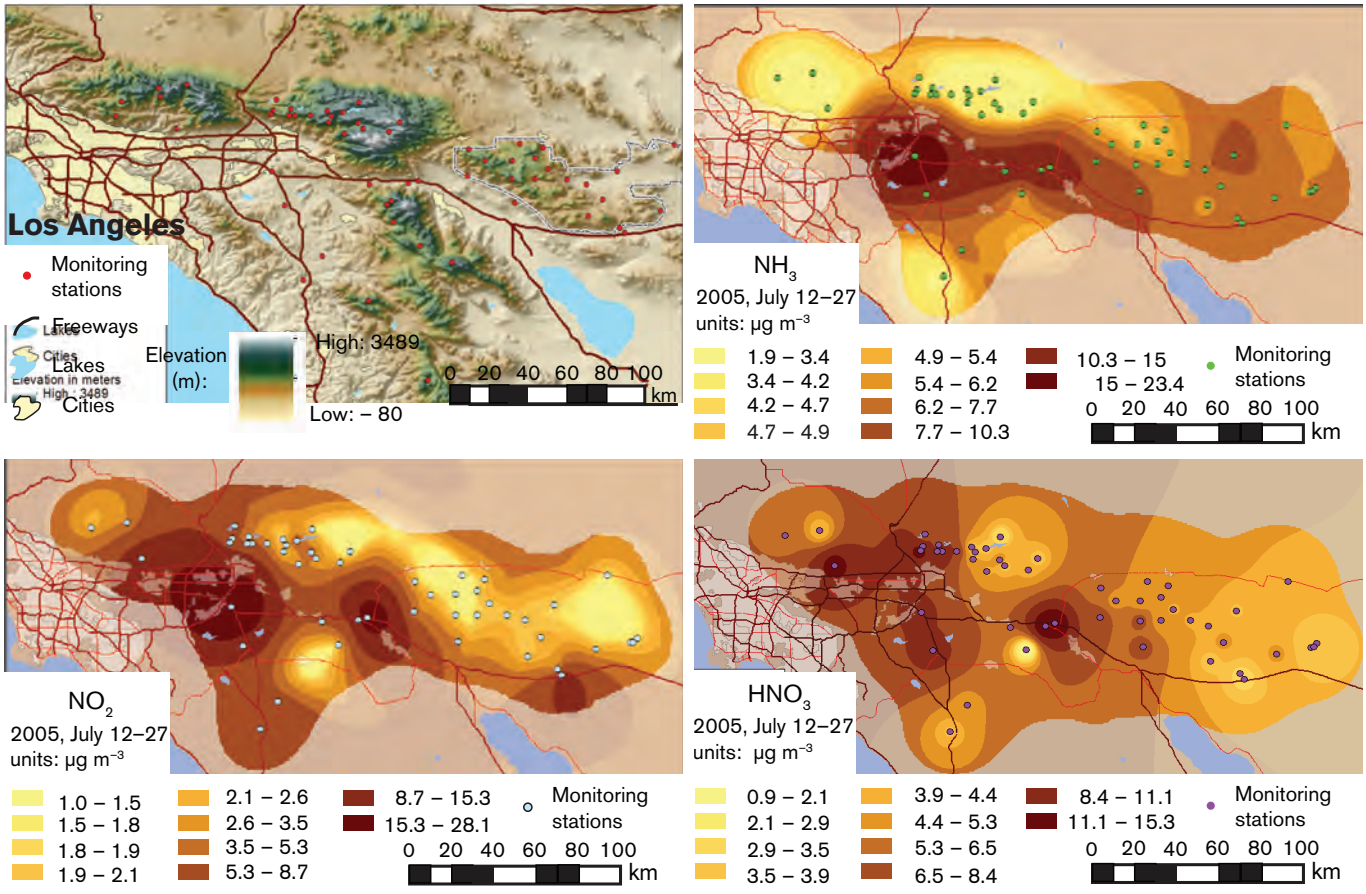

FIGURE 7.9 Nitrogenous air pollutants in southern California, summer 2005. Source: A. Bytnerowicz, unpublished.

pollutants that drive atmospheric nitrogen deposition across the landscape (Bytnerowicz et al. 2002).

High levels of ammonia and nitric acid vapor also occur on the western slopes of the Sierra Nevada Mountains near the California Central Valley (Figure 7.10). A strong gradient of both pollutants occurs across the Sierra Nevada range in the southwest-northeast direction, which coincides with the direction of prevailing winds in summer. The gradient is caused by dilution of the pollutants as they move east across the Sierras and are deposited to various surfaces and absorbed by stomatal uptake (Hanson and Lindberg 1991, Bytnerowicz and Fenn 1996). While low levels of ammonia occur in the eastern Sierra Nevada and the northern portion of the Owens Valley near Bishop and Mammoth Lakes, nitric acid vapor concentrations are elevated in the southern portion of the Owens Valley below Bishop. This may be another indication of transport of photochemical smog air masses from southern California, as with ozone (see Figure 7.7).

Ecological Effects of Nitrogen Deposition

With the possible exception of unique habitats characterized by nitrogen-bearing soil minerals (Dahlgren 1994), the natural condition of aquatic and terrestrial ecosystems in California is one of limited nitrogen availability. Chronic nitrogen deposition leads to the opposite condition: nitrogen excess. As in the case of overfertilization of crop fields, this results in leaching losses of excess nitrogen and increased emissions of nitrogenous trace gases to the atmosphere. The cardinal symptom of a forest, woodland, or chaparral ecosystem overloaded with nitrogen is elevated nitrate concentrations in surface or subsurface runoff (Fenn and Poth 1999, Fenn et al. 2008).

Nitrogen deposition can cause acidification and EUTROPHICATION effects in terrestrial and aquatic ecosystems. In California, nitrogen fertilization effects have been documented over wide areas of the state (Fenn et al. 2010), while acidification effects in terrestrial and aquatic ecosystems are of secondary importance (Shaw et al. 2014). Soils in forests and chaparral ecosystems in the Los Angeles Basin have acidified considerably since the 1970s (Fenn et al. 2011), but ecological effects of this depression in pH have not been demonstrated. This could be because these soils are high in BASE CATIONS compared to acidic and highly leached soils in the eastern U.S. and Europe, where base cation depletion has resulted from chronic atmospheric acidic deposition and leachate losses of base cations (Fenn et al. 2006).

The most widespread effects of nitrogen deposition observed in California are shifts in communities of EPIPHYTIC LICHENS in forests and chaparral/oak woodlands. OLIGOTROPHIC species are highly sensitive to atmospheric nitrogen, with initial declines in occurrence observed at nitrogen deposition levels as low as 3 kg ha^{-1} yr^{-1} (Fenn et al. 2008), a level that occurs over much of California. Biodiversity impacts to plant communities can also occur at relatively low levels of long-term nitrogen deposition. In low productivity ecosystems such as grasslands, coastal sage scrub, and desert scrub,

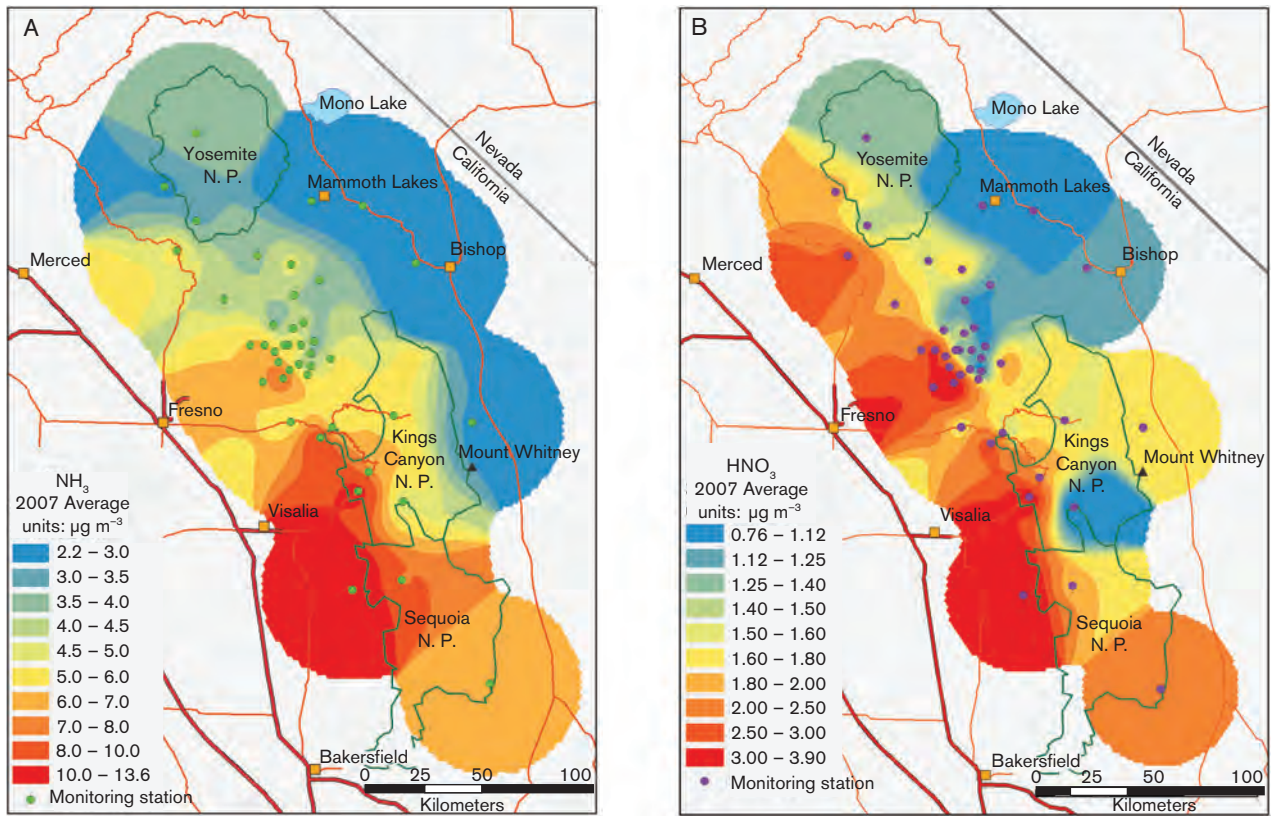

FIGURE 7.10 (A) Ammonia and (B) nitric acid vapor distribution in the southern Sierra Nevada in summer 2007. Source: A. Bytnerowicz, unpublished.

nitrogen deposition enhances the growth of invasive species, often resulting in loss of diversity and vegetation type change—sometimes as a result of increased fuel accumulation and fire occurrence (Weiss 1999, Allen et al. 2007, Fenn et al. 2010, Rao et al. 2010). Biodiversity impacts are also likely in forest understory communities subjected to elevated nitrogen deposition, though an investigation along an air pollution gradient in the San Bernardino Mountains was inconclusive due to confounding factors such as precipitation, ozone, and local disturbances (Allen et al. 2007). Effects on communities of symbiotic mycorrhizal fungi have also been shown in response to nitrogen deposition in mixed conifer forests, chaparral and coastal sage scrub vegetation of California (Egerton-Warburton and Allen 2000, Fenn et al. 2011).

In California forests exposed to elevated levels of air pollution, ozone and nitrogen deposition interact with other stressors, such as long-term fire suppression, climate change, drought stress, and bark beetle outbreaks, to affect the vigor, resilience, and sustainability of these forests. Effects are particularly acute in ponderosa and Jeffrey pine because of their sensitivity to ozone. The phytotoxic effects of ozone in combination with nitrogen enrichment result in dramatic physiological changes and increased sensitivity to bark beetle outbreaks and mortality (Jones et al. 2004, Grulke et al. 2009). Nitrogen deposition and nitrate concentrations in alpine lakes in the Sierra Nevada of California are generally lower than in the Colorado Front Range (Sickman et al. 2002, Baron et al. 2011). Nitrate concentrations in Sierran lakes begin to increase noticeably as total nitrogen deposition increases above 2 kg ha^{-1} yr^{-1} (Baron et al. 2011). Changes in DIATOMS in the sediments of two lakes in the eastern Sierra Nevada accompanied nitrogen enrichment that began in the early 1960s (Saros et al. 2011). This response has been observed with wet nitrogen deposition levels as low as 1.4 kg ha^{-1} yr^{-1}.

In a study of seven major vegetation types in California, an estimated 35% of the land area was in exceedance of CRITICAL LOADS, threshold nitrogen deposition at which harmful effects are expected to occur (Figure 7.11; Table 7.2; Fenn et al. 2010). For grasslands, coastal sage scrub, desert scrub, and pinyon-juniper woodland vegetation types, the most widespread effect of nitrogen deposition was an increase in exotic annual grasses. In grasslands and coastal sage scrub, this results in loss of native diversity and cover. In desert scrub and pinyon-juniper habitats, exotic biomass accumulation becomes sufficient to sustain fire. The most widespread effect of nitrogen deposition in forests, chaparral, and oak woodlands in California is increased nitrogen concentration in epiphytic lichens and a shift to lichen communities dominated by eutrophic species (Fenn et al. 2010). Elevated nitrate concentrations in streamwater and groundwater also occur in the chaparral, woodland, and forested watersheds most exposed to nitrogen deposition, impacting water quality in areas where the nitrogen critical load is exceeded (Fenn et al. 2010).

Other Pollutants

Atmospheric deposition of mercury (Hg) is low in California compared to the eastern U.S. (Prestbo and Gay 2009), although sampling sites are few. Localized hotspots of atmospheric mercury occur in disturbed, natural source areas, including geothermal or volcanically active regions (Nacht et al. 2004). Some studies have shown that long-range transport of pollutants from Asia contributes to mercury deposition on

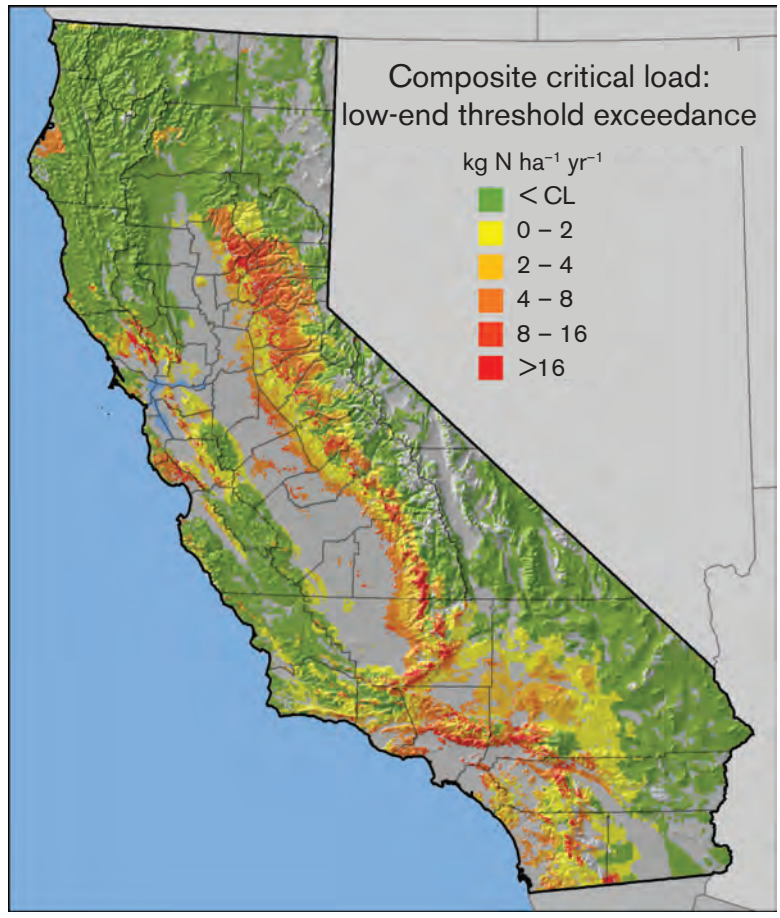

FIGURE 7.11 Exceedance values for critical loads (CL) of N deposition in California. Source: Fenn et al. 2010.

the U.S. West Coast (Weiss-Penzias et al. 2007). However, this does not result in high concentrations of atmospheric mercury in California (Prestbo and Gay 2009), so serious, widespread ecological effects caused by this pollutant are unlikely.

Sulfur dioxide emissions have been low in California because relatively little coal is used as an energy source in the state. Primary emissions of sulfur dioxide are from ships docked in ports, mobile sources, and oil refineries, but they are low and generate only local impacts. Consequently, sulfur deposition in California has historically been of little ecological significance (Cox et al. 2009). Lead (Pb) emissions to the atmosphere, from the use of leaded gasoline, increased steadily in California from the 1950s, peaked around 1970, and declined to below 1950 levels by 1982 (Mielke et al. 2010). As a result of lead phase-out regulations for gasoline, concentrations of lead in runoff from highways in California in the mid-1990s and 2000s was as much as eleven times lower than during the 1980s (Kayhanian 2012). No serious ecological impacts of lead emissions have been recently reported in California.

Long-range transport of semivolatile organic compounds (SOCs)—such as various types of pesticides, fire retardants such as polybrominated diphenyl ethers (PBDEs), polychlorinated biphenyls (PCBs), and polycyclic aromatic hydrocarbons (PAHs)—potentially have important ecological effects on high-elevation aquatic and terrestrial ecosystems of the Sierra Nevada. Measurements at the Emerald Lake and Pearl Lake area of Sequoia and Kings Canyon National Park showed significant contamination of snowpack, lake sediments, vegetation, and fish. That study also showed that Sequoia and Kings Canyon National Park had the highest concentrations of currently used pesticides among western national parks because of its proximity to agricultural sources in the Central Valley. These compounds move up the food chain, affecting health of wildlife and humans (Landers et al. 2010).

Dust, Aerosols, and Black Carbon

Dust aerosols, or particulate matter, of both natural and anthropogenic origins, play an important role in cloud formation, fertilization of oceans, supply of reaction surfaces for atmospheric chemical processes, degradation of visibility and reducing sunlight at the surface, thus affecting climate and biota as well as human health (VanCuren and Cahill 2002, Frank et al. 2007). Although many uncertainties exist in estimates of global-scale RADIATIVE FORCINGS, contribution of dust is comparable with sulfate aerosols created by industrial pollution (Tegen and Fung 1994). Aerosols of diameters between about 0.08 and 1 micrometer are the most relevant to radiative forcing of climate because of their efficiency in scattering solar radiation and their role as CLOUD CONDENSATION NUCLEI (Murphy et al. 1998). Roughly half of current global dust emissions are estimated to be of anthropogenic origin, resulting from soil degradation from activities such as agriculture, deforestation, and overgrazing (Tegen and Fung

1995, Miller and Tegen 1998). Particulate matter, in both its fine and coarse fractions, is a CRITERIA POLLUTANT with established air quality standards under the Clean Air Act.

In the California Mojave Desert the amount of dust and other particulate matter has been increasing because of anthropogenic inputs created by various land use practices (Frank et al. 2007). Dust storms occurring in the Owens Valley east of the Sierra Nevada as a result of many decades of pumping water from that aquifer to Los Angeles lead to violations of the coarse particulate matter air quality standard. The Owens Valley is one of the most turbulent valleys in the U.S. and one of the largest coarse particulate matter sources in the Western Hemisphere (Reid et al. 1994). Coarse particulate matter is generated during wind events by sandblasting of the EFFLORESCENT CRUST with saltation particles created from lakebed sediment and sand from the shoreline (Reid et al. 1994). Atmospheric coarse particulate concentrations in the Owens Valley area during windstorms can exceed 1,000 $\mu g\ m^{-3}$ (compared to the federal health standard of 150 $\mu g\ m^{-3}$), with plumes reaching above 2,000 meters in height (Reid et al. 1994).

Marine aerosols also play an important role in atmospheric processes and affect radiative forcing and climate directly by scattering and absorbing radiation and indirectly by influencing droplet-size distribution and ALBEDO of clouds in the marine boundary layer (Fitzgerald 1991). Long-range transport of polluted air masses from Asia and other remote areas also could be contributing to recent changes in mountain snow cover and related water shortages in California. Atmospheric aerosols from Asia are a regular component of the troposphere over California, particularly in spring, and a significant contributor to aerosol loading at high altitude (500–3,000 meter) remote sites across western North America. Twenty-four-hour fine particulate matter concentrations contributed from Asian aerosols range between 0.2 to 3 $\mu g\ m^{-3}$, and those of coarse particulate matter are about 5 $\mu g\ m^{-3}$ (VanCuren and Cahill 2002, VanCuren 2003). Long-rage transport of desert dust fine particles and sea salt aerosols have positive effects on the formation of cloud ice and precipitation, as documented in the northern Sierra Nevada (Rosenfeld and Givati 2006, Rosenfeld et al. 2008). Dust and biological aerosols (such as bacteria) can be transported from as far as Saharan and Asian deserts and be present in high-altitude clouds, serving as ice-formation nuclei and increasing winter snow precipitation in the Sierra Nevada (Creamean et al. 2013). In contrast, fine air pollution aerosols from densely industrialized/urbanized areas such as the San Francisco Bay and California Central Valley can reduce cloud drop effective radii and suppress downwind precipitation in the southern and central Sierra Nevada (Rosenfeld et al. 2008). Similar negative effects on cloud condensation nuclei formation and precipitation may occur downwind of emissions from wildland fires (Rosenfeld and Givati 2006).

Darkening of snow and ice by BLACK CARBON deposition is one of the main factors causing early melting of the snow pack in the Sierra Nevada. In winter, with prevailing winds from the northwest, black carbon transported from as far as Asia can contribute one-quarter to one-third of its deposition (Hadley et al. 2010). However, most black carbon deposition results from shorter-range transport of polluted air masses from California sources, such as diesel engine emissions or wood burning (Chow et al. 2010, 2011). In addition to black carbon, emissions from forest fires also contain various organic carbon molecules that contribute to the formation of haze, blocking sunlight and cooling the atmosphere (Goldammer et al. 2009). From the perspective of potential climate change effects, emissions of black and organic carbon from wildland fires counteract each other, suggesting that controlling diesel and coal-burning emissions should be the top priorities for efforts to control emissions of C compounds that contribute to climate change (Zimmer 2013).

Fire Effects on Air Quality

Fire plays a key role in the health and structure of California ecosystems (see Chapter 3, "Fire as an Ecosystem Process"). Patterns of forest fire frequency, intensity, and severity have been gradually altered by the use of fire suppression; this has contributed to conditions that favor high-intensity, destructive fires (USDA Forest Service 2001, Radke et al. 2001, Syphard et al. 2007). Wildland fires, both wild and prescribed, emit large quantities of aerosols and greenhouse gases into the atmosphere, significantly impacting climate and air quality (Zhang and Kondragunta 2008). Air pollution impacts from wildfires have been growing due to their increased size and number during the past decade (Jaffe et al. 2008), a trend expected to continue in the future (IPCC 2001).

Wildland fires involve complex combustion processes dependent on fuel loading, fire behavior, and weather conditions. Smoke from fire is composed of hundreds of chemicals in gaseous, liquid, and solid forms (Ottmar and Reinhardt 2000, Urbanski et al. 2009). Wildland fires emit substantial amounts of volatile organic compounds, carbon and nitrogen oxides, as well as directly and secondarily formed particulate matter and ozone (Cheng et al. 1998, Andreae and Merlet 2001, Pfister et al. 2008) and to a lesser extent ammonia, methane, sulfur oxides (Ward and Smith 2001, Koppmann et al. 2005), and other organic species and trace elements. Wildfire smoke can be transported for thousands of kilometers across counties, states, countries, and continents (Wotawa and Trainer 2000, Foster et al. 2001, Damoah et al. 2004, DeBell et al. 2004, Sapkota et al. 2005, Morris et al. 2006).

Forest fires impact tropospheric chemistry (Andreae and Merlet 2001) and are the dominant source of organic carbon aerosol emissions, twice as high as those resulting from the combustion of fossil fuels (DeBell et al. 2004). Forest fires also produce black carbon, which has significant human health and climate impacts, in amounts comparable to those from the burning of fossil fuels (IPCC 2001). Burning of forests also impacts global processes by releasing various greenhouse gases that affect the radiation budget as well as by emitting other scattering and absorbing aerosols (IPCC 2001). Finally, smoke from forest fires can affect the regional shortwave radiation budget and change atmospheric thermodynamics. All of these effects depend on size and intensity of the fires (Liu 2005). Particulate matter produced during catastrophic fire events is of great concern because it can adversely impact public health and be a principal cause of reduced visibility (Park et al. 2007). Smoke from wildfires can significantly increase fine particulate matter concentrations (Chandra et al. 2002, McMeeking et al. 2002, DeBell et al. 2004, Linping et al. 2006, Pfister et al. 2008) and exacerbate the already polluted air found in southern California and the California Central Valley.

While the number of forest fires and area burned have been increasing in the U.S., including California and the western states (see Chapter 3, "Fire as an Ecosystem Process"), par-

ticulate matter concentrations in selected California sites have been decreasing over the past decade. Locations in the San Francisco Bay area and mountain locations experience lower particulate matter concentrations than those in southern California and the California Central Valley. In 2008 northern California experienced a high incidence of forest fires; increased fine particulate matter concentrations in Sacramento and the southern Sierra Nevada were most likely caused by these forest fires. For particulate matter, sites closest to and downwind of the fire are the most affected. If wildfires in California continue to increase in frequency, size, and severity, fine particulate matter concentrations will likely affect both regions experiencing recent air quality improvements and areas remaining out of compliance with ambient air quality standards.

Interactive Effects of Air Pollution and Climate Change and Projections for the Future

More than one hundred years of effective fire prevention have resulted in widespread densification of forest stands, predisposing western forests to drought. Warming climates and less predictable precipitation add to soil moisture stress in California forests. In some areas, elevated ozone and nitrogen deposition levels have exacerbated drought stress and predisposed forests to bark beetle attacks (Takemoto et al. 2001), making them highly susceptible to catastrophic fires (McKenzie et al. 2009). Mixed conifer forests of the San Bernardino Mountains are a case study of such effects (Grulke et al. 2009). Although air pollution effects have been less severe in the Sierra Nevada than in the San Bernardino Mountains of southern California, the interactive effects of various abiotic and biotic stressors have affected the Sierras, particularly the southern areas. (Fenn et al. 2003, Takemoto et al. 2001). Interactive effects of air pollutants have been demonstrated for forests in the southwestern Sierra Nevada, where negative effects of ozone on tree growth (Peterson et al. 1987) have been partially offset by nitrogen deposition (Fenn et al. 2003). However, the combined effects of chronically elevated ozone concentrations and nitrogen deposition may also lead to severe perturbation of the physiology of key tree species and decreased ecosystem sustainability (Bytnerowicz et al. 2007, Fenn et al. 2003, Grulke et al. 2009).

In mixed conifer forests of southern California, where ozone effects on forests have historically been severe, recent decreases in ozone concentrations are likely to continue (Bytnerowicz, Fenn et al. 2013; Oltmans et al. 2013). Ozone will likely interact with climate change to strongly influence important ecosystem functions such as carbon sequestration and the quantity and quality of streamwater. Forest nutritional status, especially of nitrogen, can have major effects on forest responses to ozone. Simulation of future changes in these forests suggest that ozone impacts on forest growth will be closely associated with nitrogen deposition in these nitrogen-limited ecosystems. If the current trend of decreases in ozone continues, simulations indicate that tree biomass would not change significantly even under climate warming at high nitrogen deposition sites, while at low nitrogen deposition sites forest trees would recover from biomass loss in the late twenty-first century. Under scenarios of increasing ozone in the San Bernardino Mountains, tree biomass would decrease under two different nitrogen deposition projections, but much more under the medium-high emissions climate warming projection (A2) than under the low emissions (B1) projection (Bytnerowicz, Fenn et al. 2013). Similar changes can also be expected for the mixed conifer forests of the Sierra Nevada Mountains.

Human Health Effects of Key Pollutants

The Clean Air Act (CAA), a federal law passed in 1963 and last amended in 1990 (42 U.S.C. §7401 et seq.), forms the basis for national control of air pollution. The CAA was designed to "protect and enhance" the quality of the nation's air resources. Basic elements of the Clean Air Act include national ambient air quality standards (NAAQS) for criteria air pollutants (Table 7.3). In California, with regard to human health, the criteria pollutants of most importance are fine and coarse particulate matter, ozone, nitrogen dioxide, and carbon monoxide.

Long-term exposure to particulate matter causes serious human health effects (Koelemeijer et al. 2006), resulting in lower life expectancy for people living in areas with high particulate matter levels (Houthuijs et al. 2001). Negative health effects are mainly associated with fine particulate matter (WHO 2003). The adverse health effects of particulate matter include increased mortality and morbidity, reduced lung function, increased respiratory symptoms (such as chronic cough or bronchitis), aggravated respiratory and cardiovascular disease, eye and throat irritation, coughing, breathlessness, blocked and runny noses, skin rashes, and lung cancer (Radojevic and Hassan 1998, Houthuijs et al. 2001). Strong evidence suggests that fine particulate matter is more hazardous to human health because smaller particles induce more inflammation than larger particles on a mass basis. Thus epidemiological studies over the past decade have emphasized fine particulate matter (Querol et al. 2007).

Ozone is also a serious health risk. The adverse health effects associated with exposure to elevated levels of ground-level ozone include lung function decrements, airway hyper-reactivity, epithelial cell damage, and bronchoalveolar inflammation (Hayes et al. 1993). Even at relatively low levels, ozone may cause inflammation and irritation of the respiratory tract, particularly during physical activity, causing coughing, throat irritation, and difficulty breathing (EPA 2008). Ozone can increase the susceptibility of the lungs to infections, allergens, and other air pollutants, and aggravate chronic lung diseases, such as asthma, emphysema, and bronchitis. It can also reduce the immune system's ability to fight bacterial infection in the respiratory system and increase the frequency of asthma attacks (EPA 2008).

Nitrogen dioxide is a strong oxidizing agent that reacts in the air to form corrosive nitric acid vapor as well as toxic organic nitrates. It plays a major role in the atmospheric reactions that produce ground-level ozone. Nitrogen dioxide can irritate the lungs and lower resistance to respiratory infections such as influenza and enhance the effects of other environmental pollutants including allergens (WHO 2003). The effects of short-term exposure are still unclear, but long-term exposure may impair lung function and increase the risk of respiratory symptoms, and includingacute respiratory illness in children (WHO 2003). Carbon monoxide causes tissue hypoxia by preventing the blood from carrying sufficient oxygen. At low to moderate concentrations, health effects may include headache, dizziness upon exertion, fatigue, palpitations, nausea, vomiting, difficulty breath-

TABLE 7.2

Summary of critical loads (CL) and methods used to determine empirical critical loads for seven major vegetation types in California

Vegetation type	Area of vegetation cover (km^2)	Response variables for CL determination	CL values (kg N ha^{-1} yr^{-1})	References
Mixed conifer forest	106,663	Exceedance of peak streamwater NO_3^- concentration threshold (0.2 mg NO_3-N L^{-1})	17	Fenn et al. 2008
Mixed conifer forest		Enriched N in tissue of the lichen *L. vulpina* (above 1.0% N)	3.1	Fenn et al. 2008
Mixed conifer forest		Epiphytic lichen community shift away from acidophyte (oligotroph) dominance	5.2	Fenn et al. 2008
Mixed conifer forest		Extirpation of acidophytic (oligotrophic) lichens	10.2	Fenn et al. 2008
Mixed conifer forest		Fine root biomass reduction (26%) in ponderosa pine trees	17	Fenn et al. 2008
Chaparral	27,045	Exceedance of peak streamwater NO_3^- concentration threshold	10–14	Fenn et al. 2011
Chaparral and oak woodlands	59,704	Epiphytic lichen community shift to eutrophic lichen species dominance	5.5	Fenn et al. 2011, Jovan 2008, Jovan and McCune 2005
Coastal sage scrub	6,328	Decrease in native plant species and forb richness	7.8–10	Fenn et al. 2011
Coastal sage scrub		Decrease in arbuscular-mycorrhizal spore density, richness, and percentage of root infection	10	Fenn et al. 2011
Annual grassland	28,634	Exotic grass invasion	6	Weiss 1999, Fenn et al. 2010
Desert scrub	75,007	Exotic grass biomass accumulation sufficient to sustain fire	3.2–9.3	Rao et al. 2010
Pinyon-juniper	6,602	Exotic grass biomass accumulation sufficient to sustain fire	3.0–6.3	Rao et al. 2010 Fenn et al. 2010

SOURCE: Fenn et al. 2010.

ing upon exertion, impaired thinking and perception, rapid heartbeat, visual disturbance, and slow reflexes (Fierro et al. 2001). However, not all symptoms always appear and tend to become more severe as exposure and concentration increase—from a mild headache to nausea progressing to more severe cases. At very high carbon monoxide levels, unconsciousness and eventually death may result, though these levels generally can occur only in confined spaces (Fierro et al. 2001).

Although air pollution levels have decreased significantly in California, one out of three Californians lives with unhealthy air. Federal standards for ozone and fine particulate matter are still exceeded in major urban areas of the South Coast (Los Angeles), San Joaquin Valley, Sacramento, and San Diego Air Basins. While in the South Coast Air Basin 60% of the population live in areas in compliance with federal air standards, in the San Joaquin Valley Air Basin only 25% enjoy air quality that meets federal standards (Barboza 2014). Additional reductions of smog-forming air pollutants, especially nitrogen oxides and volatile organic compounds, clearly are needed to improve air quality in the unhealthiest areas in California (Table 7.3).

Conservation, Adaptation, and Mitigation

Strict and efficiently enforced air quality regulations in California have reduced risks to forests caused by ozone exposures. However, overstocked forest stands, as a result of long-term fire suppression, are highly susceptible to interactive stressors, such as elevated levels of ozone and nitrogen deposition, diseases and pests, and increasing temperatures and drought (Grulke et al. 2009). Therefore effective forest thinning, mechanical biomass removal, and carefully applied prescribed fires are important management strategies for improved resilience of California forest ecosystems. There are serious limitations in using these strategies, because of their high costs and various possible environmental risks. Prominent among these is the possibility of exceeding federal and state air pollution standards during application of prescribed fires, especially for fine and coarse particulate matter.

For some ecological effects caused by atmospheric nitrogen deposition (e.g., alteration of epiphytic lichen communities, biodiversity impacts of plant communities, enhancement of invasive species), reductions in nitrogen emissions from fossil fuel burning and agricultural activities are usu-

TABLE 7.3
California and national ambient air quality standards

Pollutant	Averaging time	Federal standards	California standards
Ozone	1-hour	None	0.07 ppm
	8-hour	0.075 ppm[A]	0.07 ppm
Inhalable particulate matter (PM_{10})	24-hour	150 µg/m^3	50 µg/m^3
Nitrogen dioxide (NO_2)	1-hour	0.100 ppm	0.180 ppm
	Annual arithmetic mean	0.053 ppm	0.030 ppm
Fine particulate matter ($PM_{2.5}$)	24-hour	35 µg/m^3	Same as federal
	Annual arithmetic mean	12 µg/m^3	Same as federal
Carbon monoxide (CO)	1-hour	35 ppm	20
	8-hour	9 ppm	Same as federal
Sulfur dioxide (SO_2)	1-hour	0.075 ppm	0.25 ppm
Lead	Rolling 3-month	0.15 µg/m^3	None
	30-day	None	1.5 µg/m^3

SOURCE: EPA 2008 and California Air Resources Board.
A. Calculated as the fourth highest concentration over a 3-year period.

ally the only effective strategy over the long term (Fenn et al. 2010). In forests and woodlands the overall strategy to manage the harmful effects of excess nitrogen is to reduce the levels of nitrogen accumulated in soil, litter, and biomass by releasing nitrogen from the ecosystem, and to use silvicultural treatments to enhance forest growth and nitrogen retention. This can be done by biomass removal, stand thinning, or by prescribed fire (Gimeno et al. 2009) and would primarily be applied in acutely impacted sites. In low-biomass scrub or grassland ecosystems in which nitrogen deposition has contributed to the establishment of exotic species invasions, mowing, herbicide treatments, or strategic application of prescribed fire are approaches that can be used to favor the recovery of native species (Cione et al. 2002, Gillespie and Allen 2004, Cox and Allen 2008, Fenn et al. 2010). Cattle grazing has been effectively used in serpentine grasslands in the San Francisco/San Jose area to manage the impacts of non-native invasive annual grasses (Weiss 1999, Fenn et al. 2010). However, the best restoration strategy will be to reduce nitrogen emissions below critical loads for negative ecosystem impacts (Pardo et al. 2011).

Chronic atmospheric nitrogen deposition to forest, woodland, or chaparral catchments leads to elevated concentrations of nitrogen in surface and subsurface runoff, primarily as nitrate, potentially affecting water quality (Fenn and Poth 1999, Fenn et al. 2003). In catchments with elevated nitrogen deposition, excess nitrogen accumulates in the system, primarily in biomass or NECROMASS. When such catchments burn, large amounts of the stored nitrogen are released; increased postfire nitrification rates result in very high nitrate concentrations in runoff (Riggan et al. 1994). Fire can be used as a management strategy for releasing a portion of the excess nitrogen accumulated from atmospheric nitrogen deposition, although water quality may be affected in the process. The capacity of prescribed fire to remove excess nitrogen is limited, however (Meixner et al. 2006), because 65% to 80% of the site nitrogen capital is stored belowground in California forests, and little belowground nitrogen is released by fire (Johnson et al. 2009, Wan et al. 2001). This emphasizes once again that the preferred and most effective long-term management strategy is to reduce emissions of reactive nitrogen to the atmosphere. In practice, reduced nitrogen deposition combined with periodic prescribed fire may be the best management approach for nitrogen-saturated catchments (Gimeno et al. 2009). Notwithstanding the sharp declines in nitrogen oxides emissions in California, nitrogen deposition in some forested regions of California remains high, underscoring the need for further reductions in emissions of ammonia and nitrogen oxides.

As described earlier, air quality in many areas of California has improved even as population has increased in the past thirty years, a result of regulatory emissions policies. Measures in California Assembly Bill 32 (Global Warming Solutions Act of 2006, AB 32) are expected to result in a substantial reduction in 2020 greenhouse gas emissions from all economic sectors through energy efficiency, renewable energy, and other technological measures. Emissions of other pollutants are predicted to also decline as a result of these measures, reinforcing downward trends in ozone, nitrogen oxides, and particulate matter (Zapata et al. 2013).

Summary

At present, negative impacts of air pollution on California ecosystems are caused mainly by elevated levels of ozone and nitrogen deposition. We emphasized air pollution effects on mixed conifer forests because the best available knowledge exists for these ecosystems. Generally, ozone air pollution in California has been improving significantly since the 1970s;

however, it still causes serious ecological and human health effects. The most serious ecological effects occur in mixed conifer forests of southern California and on the southwestern slopes of the Sierra Nevada. Ozone can be transported long distances, affecting remote areas such as Joshua Tree National Park in the Mojave Desert or the eastern Sierra Nevada.

Effects of nitrogen deposition on other ecosystems have been intensively studied in California for the past two decades. Nitrogen deposition to California ecosystems is dominated by dry deposition of ammonia and nitric acid vapor, although nitrogen deposition in fog water can also be important in montane regions. Movement of ammonia and nitric acid vapor in complex terrain, and therefore nitrogen deposition, are much more spatially restricted than ozone distribution due to the high deposition velocity of these pollutants. Consequently, steep landscape gradients of nitrogen deposition occur in California mountain ranges, with the highest potential for negative effects near emission source areas (such as the western side of the Sierra Nevada and near population centers) while remote areas remain relatively unaffected. The most sensitive indicators of harmful nitrogen deposition effects on California ecosystems include shifts in epiphytic lichen communities and lichen-tissue nitrogen in mixed conifer forests, oak woodlands, or chaparral ecosystems; and enhanced biomass of exotic grasses to levels capable of causing biodiversity changes and sustaining wildland fires in desert scrub, pinyon-juniper, and coastal sage scrub ecosystems. Increased nitrate concentrations in streamwater and groundwater from montane catchments can also result from nitrogen deposition, but the land area thus affected in California is much less than that experiencing biodiversity effects. Approximately 35% of California's land area exceeds critical loads of nitrogen deposition for these impacts in seven major vegetation types in California. Urgent need exists for large-scale evaluation of California forest health in light of the interactive effects of elevated ozone concentrations, nitrogen deposition, climate change, insects, and diseases.

Finally, particulate matter pollution is a serious health threat in California, especially in urban areas affected by emissions from mobile sources such as the Los Angeles Basin, San Francisco Bay Area, and California Central Valley. The Central Valley is also affected by particulate matter emissions from intensive agricultural activities, while vast arid areas, such as the Owens Valley, suffer from suspended dust during high wind events. Potential exceedances of the national and California particulate matter air quality standards can hinder the use of prescribed fire as a management tool in forests.

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Glossary

ADIABATIC HEATING Occurs when the pressure on the parcel of air moving downhill increases and the parcel's volume decreases; as the volume decreases, the temperature increases and its internal energy increases.

AEROSOLS Fine solid or liquid droplets dispersed in air.

ALBEDO Fraction of solar energy (shortwave radiation) reflected from Earth back into space.

AMMONIA (NH_3) A colorless gas with a characteristic pungent smell. Due to its high deposition velocity, ammonia is a major contributor to atmospheric N dry deposition.

ANABATIC WINDS Upslope winds moving up on a mountainslope facing the Sun.

ANTICYCLONE A large-scale circulation of winds around a central region of high atmospheric pressure—clockwise in the Northern Hemisphere, counterclockwise in the Southern Hemisphere.

BASE CATIONS Nonacid forming cations (positively charged ions—i.e., Ca^{+2}, Mg^{+2}, K^{+}, and Na^{+}). The higher the amount of exchangeable base cations in soil, the more acidity can be neutralized.

BLACK CARBON Compound consisting of pure carbon emitted during incomplete combustion of fossil fuels, biofuels, and biomass. It is also known as soot.

CHLOROTIC MOTTLE The minute chlorotic flecks developing on foliar surface of sensitive leaves as chloroplasts become disrupted by exposure to elevated O_3 concentrations.

CLEAN AIR ACT A U.S. federal law aimed at controlling air pollution on a national level. The original 1963 law was amended in 1970, 1977, and 1990.

CLOUD CONDENSATION NUCLEI Aerosols or small particles that act as the initial sites for condensation of water vapor into cloud droplets or cloud ice particles.

CONTINENTAL BACKGROUND (OF OZONE) The surface O_3 concentration that would be present over the U.S. in the absence of North American anthropogenic emissions.

CRITERIA POLLUTANTS Air pollutants harmful to public health and the environment regulated by the Clean Air Act with limits set by the National Ambient Air Quality Standards (O_3, CO, NO_2, SO_2, PM_{10}, $PM_{2.5}$, and Pb).

CRITICAL LOAD The quantitative estimate of atmospheric deposition (of nutritional nitrogen or acidifying compounds) below which significant harmful effects on specified sensitive elements of the environment do not occur according to present knowledge.

DIATOMS Major group of algae among the most common types of phytoplankton. A unique feature of diatom cells is that they are enclosed within a cell wall made of silica called a frustule.

EFFLORESCENT CRUST The whitish layer consisting of several minerals produced as an encrustation on the surface of soil or rock in arid regions.

EPIPHYTIC LICHENS Lichens growing on trees, which obtain necessary nutrients and moisture exclusively from the atmosphere.

EUTROPHICATION The process by which ecosystems become enriched in dissolved nutrients such as nitrogen or phosphorus that stimulate the growth of plants.

GEOSTROPHIC BALANCE The condition of winds produced when the forces of Earth's rotation and of pressure gradients are balanced. (In the Northern Hemisphere, Earth's rotation deflects winds in a clockwise direction as they blow from areas of high pressure towards areas of low pressure).

INSOLATION The rate of delivery of solar radiation per unit of horizontal surface.

LONG-RANGE TRANSPORT (OF POLLUTANTS) Atmospheric transport of air pollutants within a moving air mass for a distance greater than 100 kilometers.

NECROMASS Dead parts of living organisms—for example, the bark and heartwood of trees, litter, and the hair and claws of animals.

NITRIC ACID VAPOR Gaseous form of HNO_3 with strong phytotoxic properties; a major contributor to dry atmospheric nitrogen deposition.

NITROGEN DEPOSITION The transfer of nitrogen pollutants from the atmosphere to Earth's surface. Deposition occurs as wet (e.g., rainfall, fog, or snow) and dry (e.g., gaseous or particulate deposition).

NITROGEN OXIDES (NO_x) A sum of nitric oxide (NO) and nitrogen dioxide (NO_2).

OLIGOTROPHIC Environments or organisms (e.g., lichens) characterized by low levels of nutrients. For example, oligotrophic lichens are highly sensitive to increased levels of nitrogen deposition.

OZONE (O_3) Powerful oxidant formed from dioxygen during photochemical reactions of its precursors, NOx and VOCs. Due to its high oxidizing potential, at elevated concentrations it causes damage of mucus and respiratory tissues in mammals and plant tissues.

PARTICULATE MATTER ($PM_{2.5}$ AND PM_{10}) A complex mixture of extremely small particles (<2.5μm in diameter and <10μm) that are harmful to humans. Components include inorganic and organic chemicals, metals, and soil or dust particles.

PASSIVE SAMPLERS Devices for diffusive sampling of air that rely on diffusion of gaseous pollutants through a diffusive surface onto an adsorbent.

PESTICIDES Any substance or mixture of substances intended for preventing, destroying, or controlling any pest, including unwanted species of plants (herbicides) or insects (insecticides).

PHOTOCHEMICAL Relating to or resulting from the chemical action of radiant energy and especially light.

PHYTOTOXIC INDICES Various exposure matrixes based on concentration or a dose of pollutants to determine their potential toxicity to plants (phytotoxic potential).

RADIATIVE FORCING The difference between radiant energy received by Earth and energy radiated back to space.

SANTA ANA WINDS Strong, extremely dry downslope winds that originate inland and affect coastal southern California and northern Baja California. Santa Ana winds blow mostly in autumn and winter. They can range from hot to cold, depending on the prevailing temperatures in the source regions—the Great Basin and the upper Mojave Desert.

SCAVENGING The washout or removal of air pollutants (gases and particles) from the atmosphere by precipitation, resulting in wet deposition of the scavenged pollutants.

STOMATAL UPTAKE Cumulative stomatal flux or uptake rate (of ozone or other gas) over a period of time (e.g., day, season, year); that is, the amount of ozone molecules (moles) passing through the stomata into leaves during a specific time period.

SUBSIDENCE INVERSION A temperature inversion produced by the adiabatic warming of a layer of subsiding air.

THERMAL INVERSION Occurs when a layer of warm air settles over a layer of cooler air that lies near the ground. The warm air holds down the cool air and prevents pollutants from rising and scattering, causing severe cases of photochemical smog.

TROPOSPHERIC Occurring in the troposphere, the lowest portion of Earth's atmospheric layer, with an average depth of approximately 17 kilometers (11 miles) in the middle latitudes.

VOLATILE ORGANIC COMPOUNDS (VOCS) Organic chemical compounds whose composition makes it possible for them to evaporate under normal indoor atmospheric conditions of temperature and pressure (also referred to as "reactive organic gases").

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