



Nitrogenous air pollutants and ozone exposure in the central Sierra Nevada and White Mountains of California – Distribution and evaluation of ecological risks

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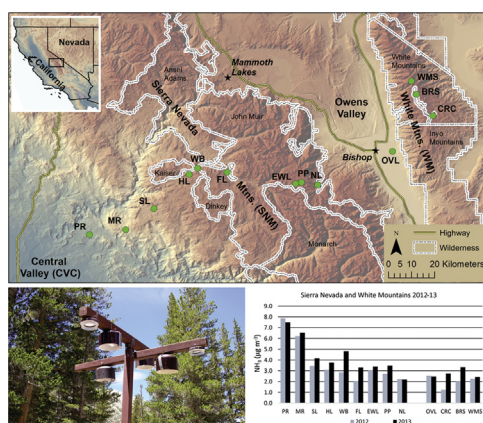
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HIGHLIGHTS

- Highly elevated NH_3 , NO_2 , and HNO_3 occurred on western slopes of SNM.
- NH_3 , NO_2 & HNO_3 in SNM reached regional background >20 km from CVC and >1500 m.
- Background levels of NH_3 , NO_2 & HNO_3 at high elevation SNM and WM were similar.
- Even lowest NH_3 levels in SNM and WM were higher than NH_3 continental background.
- Elevated O_3 and N deposition may negatively affect SNM and WM ecosystems.

GRAPHICAL ABSTRACT



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ABSTRACT

Ammonia (NH_3), nitric oxide (NO), nitrogen dioxide (NO_2), nitric acid (HNO_3), and ozone (O_3) were measured in summers of 2012 and 2013 with passive samplers. Nine monitoring sites were on W-E transect (511 to 3490 m) across central Sierra Nevada Mountains (SNM), and five sites on elevational gradient (1237 to 4346 m) in White Mountains (WM) of California. Levels of pollutants were similar in 2012 and 2013 in all sites. NH_3 , NO_2 , and HNO_3 were highest near highly polluted Central Valley of California (CVC): maximum summer season means $7.8 \mu\text{g m}^{-3}$, 3.0 ppb, and $3.0 \mu\text{g m}^{-3}$, respectively. Regional background for NH_3 , NO_2 , and HNO_3 in SNM occurred >20 km from CVC and >1500 m with seasonal averages: $2.1\text{--}4.8 \mu\text{g m}^{-3}$; $0.8\text{--}1.7 \text{ ppb}$; $1.0\text{--}1.8 \mu\text{g m}^{-3}$, respectively, during two seasons. Levels of NH_3 , NO_2 , and HNO_3 in WM remote locations were similar: $1.2\text{--}3.3 \mu\text{g m}^{-3}$, $0.6\text{--}1.1 \text{ ppb}$, and $1.0\text{--}1.3 \mu\text{g m}^{-3}$, respectively. Seasonal mean O_3 (38–60 ppb) in SNM did not change with distance from CVC nor elevation. In WM, O_3 and NO mixing ratios were 41–61 ppb and 2.3–4.1 ppb, respectively, increasing with elevation. Even the lowest NH_3 concentrations determined in this study were higher than NH_3 continental background. This fact, as well as high values of $\text{N}_{\text{reduced}}/\text{N}_{\text{oxidized}}$ near CVC of 1.9 in 2012 and 2.0 in 2013, decreasing with distance to 0.7 in 2012 and 0.8 in 2013, show importance of NH_3 emissions from CVC as a contributor to N deposition and ecological impacts in SNM. The phytotoxic O_3 indices, AOT40 and W126, for

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selected sites on SNM and WM transects, showed high potential for negative O₃ impacts on vegetation, including forest trees.

Capsule: Elevated NH₃, NO₂, and HNO₃ on the western slopes of the Sierra Nevada Mountains (SNM) near the Central Valley of California (CVC) decreased with distance from CVC and elevation to regional background levels also recorded at high elevation sites of the White Mountains (WM).

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1. Introduction

Ammonia (NH₃), nitric oxide (NO), nitrogen dioxide (NO₂), nitric acid (HNO₃), and nitrous acid (HONO) are important components of reactive nitrogen (N_r) which is responsible for significant environmental and ecological changes worldwide (Galloway et al., 2008; USEPA, 2012). In California, concentrations of these gases in air pollution source areas, such as the Los Angeles Basin or Central Valley of California (CVC), and downwind from them, are among the highest in the United States (USEPA, 2012; Bytnerowicz et al., 2016). Atmospheric deposition of elevated N_r causes eutrophication and acidification of sensitive California ecosystems (Fenn et al., 2010; Bytnerowicz et al., 2016). Ozone (O₃) is a strong oxidant and a phytotoxic air pollutant affecting the health of sensitive trees, such as ponderosa (*Pinus ponderosa* Dougl. ex Laws.) or Jeffrey (P. jeffreyi Grev. & Balf.) pines, in California mountain forests (Miller et al., 1963; Miller and Millecan, 1971; Miller, 1992). At elevated concentrations, NO₂ and O₃ have adverse effects on human health, and therefore their ambient concentrations are regulated by the National Ambient Air Quality Standards (NAAQS), and California Ambient Air Quality Standards (CAAQS) (<https://www.epa.gov/criteria-air-pollutants>; <https://www.arb.ca.gov/research/aaqs/caaqs/caaqs.htm>). Ammonia, NO_x, and HNO₃ also contribute to particulate matter (PM_{2.5}) formation, which at high concentrations affects human health and visibility (USEPA, 2012). Concentrations of all these pollutants are elevated in the CVC and in Southern California (Chow et al., 1998; Schiferl et al., 2014).

Ambient levels of air pollutants and their distribution depend on geographic location and distance from emission sources, emission rates of primary pollutants (e.g., NH₃, NO, NO₂), rates of chemical reactions leading to generation of secondary pollutants (e.g., O₃, HONO, HNO₃), and various meteorological, climatic and topographic factors as well as deposition rates (Finlayson-Pitts and Pitts, 2000; Seinfeld and Pandis, 1998). In the Mediterranean climate of California, dry atmospheric deposition of gases and aerosols in summer provides a significant portion of N_r input to ecosystems (Bytnerowicz and Fenn, 1996; Bytnerowicz et al., 1999a, 1999b).

In California some of the highest ambient concentrations of nitrogenous gaseous pollutants and N_r deposition occur on the western slopes of the Sierra Nevada Mountains (SNM), downwind and east of CVC (Bytnerowicz et al., 2016). SNM is the largest and highest mountain range in California in the form of a tilted fault block extending 640 km from south to north with a width of about 100 to 130 km, with Mount Whitney (4418 m) as its highest peak (Storer and Usinger, 1963; Schoenherr, 1992). During June through September, northwestern winds in the southern portion of CVC move polluted air masses into western slopes of SNM (Hayes et al., 1992 <https://www.arb.ca.gov/research/apr/reports/I013.pdf>). Warm, boundary layer air masses overlying CVC are stratified by a weak thermal inversion at 1000 to 1300 m. Daytime land heating generates local anabatic winds from the southwest and west along the western SNM slopes, moving polluted air masses eastward into the SNM crest. Boundary layer air funnels through low passes in SNM, while moving into the Mojave Desert and the Great Basin (Minnich and Padgett, 2003). A SNM-wide 1999 summer study showed the highest O₃ levels on the southwestern slopes of the range. Occasional transport of highly O₃-polluted air masses with strong

southwestern winds along the San Joaquin River drainage into the eastern side of SNM was also detected (Frączek et al., 2003). Along the same drainage, long-range transport of NH₃, NO₂, and HNO₃ was observed, with highest concentrations near the CVC pollution source area, which gradually decreased with distance along the northeastern direction (Cisneros et al., 2010). A strong west-to-east gradient of NH₃, NO₂, and HNO₃ was recorded in summer 1999 on the western slopes of the central SNM in Sequoia National Park (Bytnerowicz et al., 2002). However, distributions of NH₃, NO, NO₂, HNO₃, and O₃ at high elevation sites traversing the SNM, including sites located above the CVC inversion layer, and within the John Muir and Ansel Adams Wilderness areas, have not been characterized.

While O₃ distributions in the second highest range in California, the White Mountains (WM), have been characterized (Burley and Bytnerowicz, 2011), information on distribution of N_r gases in that mountain range is lacking. The White Mountains are a triangular fault-block mountain range facing SNM across the upper Owens Valley, extending for approximately 97 km south to north as a greatly elevated plateau. This plateau is about 32 km wide on the south, narrowing to a point at the north, and with elevations generally increasing south to north, with the White Mountain Summit (4342 m) as its highest point. The WM are the highest range completely inside the Great Basin. The entire WM range is within the Inyo National Forest and most of it has special protection designation as a Wilderness area ([https://en.wikipedia.org/wiki/White_Mountains_\(California\)](https://en.wikipedia.org/wiki/White_Mountains_(California))). In July and August, the town of Bishop located in the Owens Valley just below WM receives southeast winds bringing polluted air masses from the Los Angeles Air Basin (Hayes et al., 1992; <https://www.arb.ca.gov/research/apr/reports/I013.pdf>).

Knowledge on background levels of air pollutants in remote areas is essential as a reference for areas affected by anthropogenic activities. Such information is also crucial for enforcing the NAAQS and evaluation of potential risks to human and ecosystem health. In this regard, information on NH₃, NO, NO₂, HNO₃, and O₃ concentrations in remote and high elevation areas of SNM and WM is of high importance for these two California mountain ranges, as well as other mountainous areas in North America, the northern Hemisphere, and worldwide. This paper presents information on ambient concentrations of these pollutants as well as their distribution along high elevation transects in SNM and WM. These transects include several federally protected wilderness areas for which air quality related values (AQRV) (U.S. Forest Service, National Park Service, and U.S. Fish and Wildlife Service, 2010) are essential. Therefore, we also estimated potential impacts of air quality on sensitive ecosystem endpoints.

1.1. Objectives

- Determine levels of gaseous air pollutants (O₃, NH₃, NO, NO₂, and HNO₃) in high elevation areas of SNM and WM.
- Evaluate the influence of CVC pollution source area on spatial distribution of the measured pollutants.
- Establish “background” levels of the measured pollutants for California mountainous remote areas.
- Evaluate potential ecological impacts of N air pollutants, N deposition, and ozone.

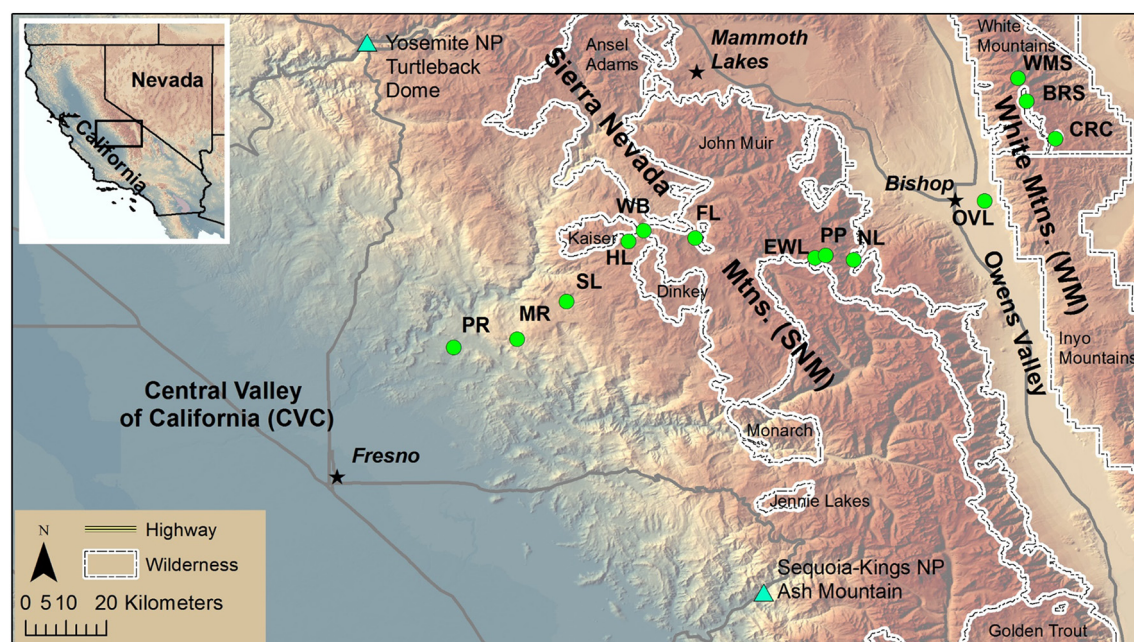


Fig. 1. Monitoring networks: W-E transect through the Sierra Nevada Mountains starting at the eastern edge of the Central Valley of California at Prather (PR) and ending at the western edge of the Owens Valley at North Lake (NL), and the transect in the White Mountains starting at the Owens Valley Laboratory (OVL) and ending at the White Mountain Summit (WMS).

2. Methodology

Passive air pollution samplers have been used to meet the above objectives. It has been established in numerous studies that these devices are useful for monitoring ambient air pollutant concentrations in remote areas (Krupa and Legge, 2000; Fenn et al., 2018).

Nine air pollution monitoring sites were established across SNM on a west - east (W-E) transect and five sites on an elevational gradient in WM of California. The SNM transect, ranging in elevation from 511 to 3490 m, started at Prather at the eastern edge of CVC and ended at North Lake on the eastern side of SNM. The WM elevational transect, ranging in elevation from 1237 to 4346 m, consisted of the Owens Valley Laboratory (OVL) near Bishop, plus three high elevation sites

(Crooked Creek, Barcroft Station, White Mountain Summit). For comparison, NH_3 and HNO_3 seasonal and annual concentrations were obtained from the CASTNET/AMoN sites at Turtleback Dome, Yosemite National Park, and Ash Mountain, Sequoia & Kings Canyon National Park (Fig. 1). Site coordinates, elevation, distance from the starting point for SNM transect, as well as N deposition estimates are provided in Table 1. Passive samplers for determination of ambient concentrations of air pollutants were placed on a wooden pole about 2 m above the ground. The sampler assembly included samplers for ozone (O_3), ammonia (NH_3), nitrogen dioxide (NO_2), nitrogen oxides (NO_x), and nitric acid (HNO_3). Two replicate samples were collected for O_3 , NH_3 , NO_2 , and NO_x , and three replicate samples were collected for HNO_3 at each site. Measurement sites were carefully selected to ensure good exposure

Table 1
Monitoring sites on the Sierra Nevada Mountains and White Mountains transects: geographic coordinates, distance from the starting point of the transect (Prather), and elevation.

ID	Site name	Latitude	Longitude	Distance east of Prather (km)	Elev. (m)	CMAQ Wet Dep. (kgN/ha/yr)	CMAQ Dry Dep. (kgN/ha/yr)	CMAQ N Total Dep. (kgN/ha/yr)
Sierra Nevada Transect								
PR	Prather	37.03564	-119.51218	0	511	1.85	3.30	5.15
MR	Mountain Rest	37.05421	-119.37119	12.6	1252	1.67	3.11	4.78
SL	Shaver Lake	37.13671	-119.26059	22.6	1719	1.62	2.61	4.22
HL	Huntington Lake	37.27059	-119.12383	35.1	2588	0.85	1.89	2.75
WB	White Bark	37.29433	-119.09046	38.1	2912	0.85	1.89	2.75
FL	Florence Lake	37.27827	-118.97511	48.3	2280	1.08	1.53	2.60
EWL	East Wahoo Lake	37.23391	-118.70826	71.9	3447	1.66	1.48	3.13
PP	Piute Pass	37.23950	-118.68429	74.0	3490	1.66	1.48	3.13
NL	North Lake	37.22935	-118.62182	79.6	2863	1.66	1.48	3.13
White Mountains Transect								
OVL	Bishop - OVL	37.3602	-118.3297		1237	0.45	1.21	1.66
CRC	Crooked Creek	37.4991	-118.1718		3100	1.11	1.43	2.54
CRC-R	Crooked Creek Ridge (active only)	37.5001	-118.1672		3231	1.11	1.43	2.54
BRS	Barcroft Station	37.5827	-118.2364		3778	1.66	1.45	3.11
WMS	White Mtn. Summit	37.6342	-118.2556		4346	1.54	1.40	2.95
CASTNET Air Quality Sites								
TB	Turtleback Dome (YOSE)	37.713251	-119.706196		1605	1.20	2.41	3.60
AM	Ash Mountain (SEKI)	36.489469	-118.829153		510	1.69	4.24	5.93

Table 2
Periods of passive air pollution monitoring within the Sierra Nevada and White Mountains transects.

ID	Site name	2012 Start date	2012 End date	2013 Start date	2013 End date
Sierra Nevada Transect					
PR	Prather	6/13/12	9/19/12	6/18/13	9/25/13
MR	Mountain Rest	6/13/12	9/19/12	6/18/13	9/25/13
SL	Shaver Lake	6/13/12	9/19/12	6/18/13	9/25/13
HL	Huntington Lake	6/26/12	9/18/12	6/18/13	9/24/13
WB	White Bark	6/13/12	9/18/12	6/19/13	9/24/13
FL	Florence Lake	6/13/12	9/18/12	6/18/13	9/24/13
EWL	East Wahoo Lake	7/24/12	9/18/12	6/18/13	9/24/13
PP	Piute Pass	6/14/12	9/18/12	6/18/13	9/24/13
NL	North Lake	6/26/12	9/18/12	6/18/13	9/24/13
White Mountains Transect					
OVL	Bishop - OVL	6/13/12	9/18/12	6/19/13	9/25/13
CRC	Crooked Creek	6/15/12	9/20/12	6/19/13	9/25/13
BRS	Barcroft Station	6/14/12	9/19/12	6/19/13	9/25/13
WMS	White Mtn. Summit	6/14/12	9/19/12	6/19/13	9/24/13

to the incoming air masses. The samplers were exchanged every 14 days in the summers of 2012 and 2013 according to the starting and ending dates shown in Table 2.

Ogawa passive samplers were used for monitoring ambient O_3 (Koutrakis et al., 1993a). Each O_3 sampler contained two cellulose filters coated with nitrite (NO_2^-) which is oxidized by O_3 to NO_3^- and analyzed with ion chromatography. The rate of NO_3^- formation (amount of NO_3^- formed on a filter over time of exposure) serves as a measure of the O_3 mixing ratios. Averaged O_3 mixing ratios determined with passive samplers were compared with real-time O_3 mixing ratios obtained with portable UV absorption 2B Technologies monitors (Bognar and Birks, 1996) on a subset of sites. Empirically derived coefficients were used for calculating O_3 mixing ratios from passive samplers. The precision of the O_3 passive samplers measured as the coefficient of variation (CV) of replicate samples for the entire study was 3%.

Ogawa passive samplers (Roadman et al., 2003), with two replicate filters coated with citric acid, were used for NH_3 monitoring. Ammonia reacts with citric acid on the filters producing ammonium citrate. After water extraction, NH_4^+ concentrations in filter extracts was determined colorimetrically on a TRAACS 2000 Autoanalyzer. Ambient NH_3 concentrations were calculated based on comparison of passive samplers against co-located honeycomb denuder systems (Koutrakis et al., 1993b). Ogawa passive samplers were also used for monitoring NO_2 and NO_x . Each NO_2 sampler contains two replicate filters coated with triethanol-amine (TEA) and each NO_x sampler consists of two replicate filters coated with TEA and 2-phenyl-4,4,5,5-tetramethylimidazoline-1-oxyl 3-oxide (also known as PTIO) as an oxidizer (Ogawa USA Inc., 2006). Both NO_2 and NO_x were collected as NO_2^- which was extracted in water and determined on a TRAACS Analyzer, and their ambient mixing ratios were calculated using calibration against Monitor Labs 8440 instruments (Alonso et al., 2005). From the difference between NO_x and NO_2 mixing ratios, NO mixing ratios were calculated.

Passive samplers developed by Bytnerowicz et al. (2005) were used for HNO_3 measurements. In the HNO_3 sampler, ambient air passes through a Teflon membrane and gaseous HNO_3 is absorbed on a Nylasorb nylon filter as NO_3^- . Nitrate concentrations in sample extracts were analyzed by ion chromatography. Concentrations of HNO_3 were determined based on calibration curves developed by comparing NO_3^- absorbed by Nylasorb sampler filters against HNO_3 concentrations determined with honeycomb denuder systems (Koutrakis et al., 1993b; Bytnerowicz et al., 2005). The precision of the NO_x , NO_2 , NH_3 , and HNO_3 passive samplers measured as the CV of replicate samples for the entire study was 7, 10, 12, and 9%, respectively.

Estimated total (wet + dry) annual N deposition fluxes for all the sites along the two transects used in this study were obtained from the Community Multi-scale Air Quality (CMAQ) model (Byun and

Schere, 2006). Grid scale resolution for the model is 12×12 km. Model results for the year 2012 (CMAQ version 2012 12 km CONUS BiDi-CAFO run of September 2014_v2) for each of the sites were downloaded from the USEPA website: http://newftp.epa.gov/exposure/CMAQ/V5_0_2/deposition_shapefiles/conus. These estimated total N deposition fluxes, in conjunction with atmospheric pollutant concentrations, were used for evaluation of their potential ecological impacts, including direct phytotoxic effects, impacts on lichen and vegetation communities, and eutrophication and acidification effects on high-elevation lakes.

Real time measurements of O_3 mixing ratios with 2B Technologies monitors (Bognar and Birks, 1996) were performed on a subset of passive sampler sites. On the SNM transect they were conducted in two years on the western portion of the transect at PR, MR, SL, HL, and WB, and additionally in 2013 at FL. On the WM transect they were conducted in both years at BRS and WMS, and at CRC-R in 2012. At the two highest WM sites (WMS, BRS) the active ozone monitors were effectively co-located with the passive samplers, but at the Crooked Creek site the active monitor (CRC-R) was located on a ridge top slightly to the east of the passive samplers (CRC). For those sites where real-time O_3 mixing ratios were measured, selected metrics for evaluation of the O_3 phytotoxic effects were calculated as 3-month and 12-h daytime values (8:00–19:59). Only those sites presenting completeness of data >80% were considered. SUM00 is a cumulative dose of all O_3 concentrations (Musselman et al., 2006). AOT40 is the accumulation of hourly mean values above 0.04 ppm (40 ppb), with values of 3.00 ppm-hours or greater having negative effects on above-ground biomass of semi-natural and natural vegetation dominated by annuals (CLRTAP, 2017). W126 is a cumulative seasonal sum of sigmoidal weighted daytime O_3 hourly values with a cumulative seasonal (3-year average) of 17.00 ppm-hours set to be sufficient to protect vegetation from O_3 exposures (US Federal Register, 2015).

3. Results

3.1. Distribution of ambient NH_3 , NO , NO_2 , HNO_3 , and O_3

Air pollution results are presented as: (1) tables with basic statistics and presentation of significance of differences between individual sites; and (2) bar graphs helping to visualize spatial trends for the combined transects. Generally, values of the measured pollutants at all SNM and WM monitoring sites were similar in 2012 and 2013 (Tables 3 and 4; Figs. 2–5). Seasonal means of NH_3 , NO_2 , and HNO_3 were significantly higher at PR and MR than in the remaining sites. The highest values recorded at PR were: NH_3 –7.8 $\mu g\ m^{-3}$ in 2012 and 7.5 $\mu g\ m^{-3}$ in 2013; NO_2 –3.0 ppb in 2012 and 2.7 ppb in 2013, HNO_3 –3.0 $\mu g\ m^{-3}$ in 2012 and 2.9 $\mu g\ m^{-3}$ in 2013.

Beyond a distance of 20 km from CVC and above 1500 m, seasonal mean NH_3 , NO_2 , and HNO_3 values were significantly lower than at the PR and MR sites, and as low as 2.1 $\mu g\ m^{-3}$ (2012) and 2.2 $\mu g\ m^{-3}$ (2013) for NH_3 ; 0.8 ppb (2012) and 1.1 ppb (2013) for NO_2 ; and 1.0 $\mu g\ m^{-3}$ (2012 and 2013) for HNO_3 (Tables 3 and 4). Spatial distribution of pollutants on the SNM transect followed polynomial regression with high R^2 values (Figs. A-1 through A-3).

In the SNM the NO seasonal means were 2.1–3.4 ppb in 2012, and 2.0–3.3 ppb in 2013. There was a trend of increasing values with elevation and distance from CVC, but it was not statistically significant (Tables 3 and 4).

Ranges of two-week averages in SNM for all sites and monitoring periods in 2012 and 2013 were: NH_3 (0.4–11.4 $\mu g\ m^{-3}$); NO (0.1–5.3 ppb); NO_2 (0.3–4.5 ppb); and HNO_3 (0.4–3.7 $\mu g\ m^{-3}$) (Tables 3 and 4).

As observed in the SNM, seasonal mean and two-week average values of the monitored air pollutants at all WM sites were similar in 2012 and 2013. Seasonal means for NH_3 were between 1.2 and 2.5 $\mu g\ m^{-3}$ in 2012, and 2.4 and 3.3 $\mu g\ m^{-3}$ in 2013; for NO between 2.3 and 4.0 ppb

Table 3

Means, standard deviation and ranges of the measured air pollutants in the Sierra Nevada Mountains and White Mountains in 2012. Different letters in each column indicate statistically significant differences between monitoring sites.

	NH ₃ (μg m ⁻³) p < .001	NO (ppb) NS	NO ₂ (ppb) p < .001	HNO ₃ (μg m ⁻³) p < .001	Ozone (ppb) p < .001
Sierra Transect					
PR	7.8 (1.5) 5.2–9.6a	2.1 (1.3) 0.2–4.6	3.0 (0.7) 2.4–4.3a	3.0 (0.3) 2.5–3.3a	56 (5) 49–61abc
MR	6.2 (1.9) 4.0–9.0a	2.3 (1.0) 0.9–3.6	2.2 (0.4) 1.8–2.8ab	2.3 (0.7) 1.6–3.5ab	60 (6) 51–65a
SL	3.5 (0.8) 2.2–4.6b	2.8 (1.1) 1.6–4.6	1.6 (1.0) 1.0–3.8bc	1.4 (0.5) 0.4–1.8bc	44 (10) 34–63c
HL	3.1 (1.4) 1.4–5.6bc	2.9 (1.3) 0.7–4.8	1.1 (0.6) 0.5–1.9bc	1.6 (0.8) 0.9–2.9bc	54 (5) 47–60abc
WB	2.8 (1.7) 0.4–5.7bc	3.2 (1.0) 2.1–4.7	0.9 (0.2) 0.6–1.2c	1.8 (0.7) 1.0–2.5bc	56 (4) 51–60abc
FL	2.1 (0.8) 1.5–3.5bc	3.2 (0.7) 2.1–4.2	1.0 (0.3) 0.5–1.4c	1.0 (0.2) 0.7–1.2c	49 (5) 42–55abc
EWL	3.1 (0.5) 2.6–3.6bc	3.0 (2.0) 0.1–4.5	0.8 (0.5) 0.3–1.4c	1.2 (na)	51 (5) 44–56abc
PP	2.7 (1.1) 0.7–4.1bc	3.4 (0.3) 3.0–3.9	1.7 (1.4) 0.5–4.5bc	1.5 (0.8) 0.7–2.9bc	58 (5) 50–63ab
NL	2.2 (0.9) 1.1–3.3bc	2.9 (0.9) 1.2–3.6	1.1 (0.6) 0.5–2.1bc	1.7 (0.9) 0.9–2.9bc	53 (6) 42–62abc
White Mountains Transect					
OVL	2.5 (1.0) 1.3–4.0bc	2.3 (0.5) 1.8–3.0	1.0 (0.4) 0.4–1.6bc	1.2 (0.2) 1.0–1.4bc	46 (8) 35–54bc
CRC	1.2 (0.3) 0.8–1.5c	4.0 (1.1) 2.5–5.7	1.1 (0.5) 0.5–1.8bc	1.0 (0.3) 0.7–1.3c	46 (8) 35–57bc
BRS	2.0 (0.8) 1.1–3.3bc	2.8 (0.9) 1.4–4.0	1.1 (0.5) 0.4–2.0bc	1.1 (0.3) 0.7–1.4c	56 (10) 43–76abc
WMS	2.3 (0.8) 0.7–3.2bc	3.4 (0.8) 2.8–5.2	0.6 (0.4) 0.2–1.2c	1.2 (0.3) 0.9–1.5bc	61 (7) 50–71a

in 2012, and 2.3 and 4.1 ppb in 2013; for NO₂ between 0.6 and 1.1 ppb in 2012, and 0.8–1.1 ppb in 2013; and for HNO₃ between 1.0 and 1.2 μg m⁻³ in 2012, and 1.1 and 1.3 μg m⁻³ in 2013 (Tables 3 and 4, Figs. 2–5). Ranges of two-week averages in WM for all sites and monitoring periods in 2012 and 2013 were: NH₃ (0.3–5.9 μg m⁻³); NO (1.1–5.7 ppb); NO₂ (0.2–2.0 ppb); HNO₃ (0.7–2.0 μg m⁻³) (Tables 3 and 4).

On the SNM transect the O₃ two-week average mixing ratios ranged between 34 and 65 ppb in 2012, and 34 and 64 ppb in 2013, while its seasonal means were between 44 and 60 ppb in 2012, and 38 and 56 ppb in 2013. Ozone mixing ratios did not significantly change with distance from CVC or elevation. In both years, the lowest O₃ seasonal means were at SL – 44 ppb in 2012 and 38 ppb in 2013. On the WM transect, the two-week O₃ average mixing ratios were between 35 and 76 ppb in 2012, and 35 and 81 ppb in 2013. The O₃ seasonal means ranged between 46 and 61 ppb in 2012, and 41 and 59 ppb in 2013 (Tables 3 and 4). The O₃ mixing ratios in WM significantly increased with elevation in both years (Fig. A-4).

Real-time O₃ mixing ratios were measured with 2B Technologies instruments in selected locations on both transects and recorded as 1-h averages (Table A-1). Seasonal means of such values in two seasons for various sites were between 36.4 ppb at OVL in 2013 and 63.0 ppb at MR in 2012. Minimal 1-h values were between 2.7 ppb at SL in 2013 and 36.2 ppb at CRC-R in 2012 while their maxima oscillated between 70.2 ppb at CRC-R in 2012 to 186.8 ppb at SL in 2013.

Seasonal means of 1-h averages for those selected sites were used for developing curves of diurnal O₃ changes. On the western portion of the SNM transect, O₃ mixing ratios differed between the sites and were highly variable in time. In all sites the lowest diurnal average values occurred early morning and the highest in the afternoon. Highest values among all sites of 76 and 75 ppb were recorded at MR at 1600 PST in 2012 and 1500 in 2013, respectively, while slightly lower values were recorded at PR an hour earlier (74 ppb in 2012 and 68 ppb in 2013). The lowest values, near 40 ppb, were determined early morning (0600–0700 PST) in both years at PR and FL. The least variable diurnal changes were at WB – between 51 and 65 in 2012 and 51 and 57 in 2013 (Fig. A-5). The diurnal O₃ changes were much less pronounced on the WM transect and were relatively flat with minimal differences between the nighttime and daytime values. The BRS diurnal values oscillated between 55 and 57 ppb in 2012, and 51 and 53 ppb in 2013. Those at WMS were higher, between 59 and 62 in 2012, and 56 and 60 ppb in 2013 (Fig. A-6).

3.2. Ozone phytotoxic indices

These indices were calculated only for sites and years for which sufficient real-time O₃ hourly data was available (Table A-2). On the SNM transect in 2013, the SUM0 index ranged between 50.21 and 63.58 ppm h. The AOT40 values ranged between 14.11 and

Table 4

Means, standard deviation and ranges of the measured air pollutants in the Sierra Nevada Mountains and White Mountains in 2013. Different letters in each column indicate statistically significant differences between monitoring sites.

	NH ₃ (μg m ⁻³) p < .001	NO (ppb) p < .001	NO ₂ (ppb) p < .001	HNO ₃ (μg m ⁻³) p < .001	Ozone (ppb) p < .001
Sierra Transect					
PR	7.5 (2.8) 3.7–11.4a	2.0 (1.0) 0.1–3.1b	2.7 (0.7) 1.7–3.8a	2.9 (0.6) 2.3–3.7a	50 (6) 44–60abcd
MR	6.5 (1.7) 4.0–9.7ab	2.3 (0.7) 1.2–3.2ab	2.2 (0.3) 1.8–2.6ab	2.2 (0.7) 1.5–3.2a	54 (5) 49–64ab
SL	4.2 (0.9) 3.1–5.5bc	2.0 (0.9) 0.8–3.4b	1.5 (0.5) 0.8–2.1bc	1.2 (0.2) 1.1–1.5b	38 (3) 34–43d
HL	3.7 (0.8) 2.5–4.9c	2.4 (1.2) 0.7–3.7ab	1.3 (0.9) 0.5–3.0bc	1.3 (0.5) 0.7–2.2b	49 (7) 40–62abcd
WB	4.8 (1.7) 3.4–8.2abc	2.1 (1.2) 0.2–4.0b	1.4 (0.9) 0.3–2.6bc	1.4 (0.5) 0.9–2.2b	52 (5) 45–58abc
FL	3.3 (2.0) 1.4–7.0c	2.7 (1.2) 1.5–5.1ab	1.2 (0.4) 0.5–1.7bc	1.1 (0.3) 0.6–1.4b	45 (4) 40–50bcd
EWL	3.4 (0.9) 2.3–4.8c	3.3 (1.0) 2.4–5.3ab	1.1 (0.4) 0.5–1.8c	1.1 (0.4) 0.7–1.9b	50 (4) 45–56abc
PP	3.5 (0.9) 2.7–4.8c	2.8 (1.3) 1.1–4.6ab	1.1 (0.8) 0.4–2.6c	1.2 (0.3) 0.8–1.5b	56 (4) 51–61ab
NL	2.2 (1.3) 0.4–4.7c	2.3 (1.1) 0.6–3.8ab	1.2 (0.5) 0.6–2.1bc	1.0 (0.2) 0.6–1.3b	50 (5) 41–55abcd
White Mountains Transect					
OVL	2.5 (0.9) 1.9–4.4c	2.3 (0.9) 1.1–3.8ab	1.0 (0.4) 0.4–1.4c	1.1 (0.3) 0.8–1.5b	41 (4) 35–45cd
CRC	2.7 (0.8) 1.7–3.9c	3.7 (1.0) 2.2–5.1ab	1.1 (0.6) 0.4–1.8c	1.3 (0.4) 0.9–2.0b	47 (11) 35–60bcd
BRS	3.3 (1.3) 2.3–5.9c	4.1 (0.8) 2.9–4.9a	0.8 (0.4) 0.4–1.6c	1.1 (0.2) 0.9–1.4b	51 (5) 43–55abc
WMS	2.4 (1.5) 0.3–4.6c	3.8 (0.9) 2.8–5.3ab	0.9 (0.3) 0.5–1.2c	1.1 (0.4) 0.7–1.8b	59 (12) 45–81a

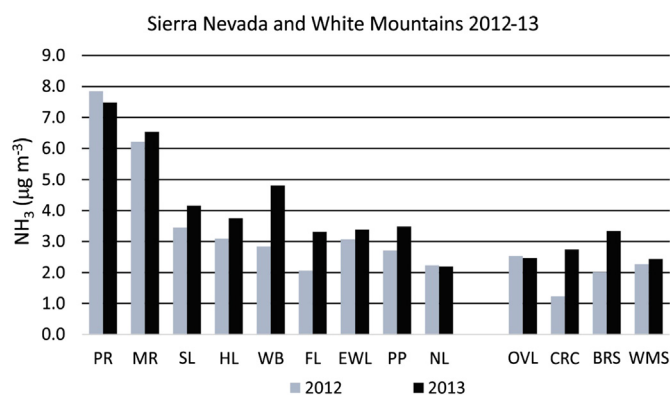


Fig. 2. Seasonal average NH_3 concentrations on the W-E Sierra Nevada transect and White Mountains elevational transect in 2012 and 2013.

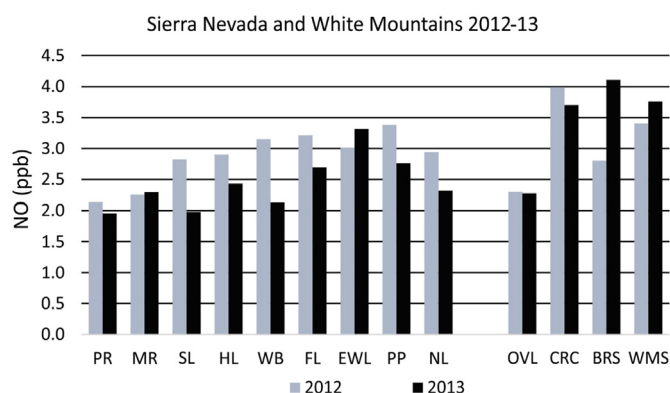


Fig. 3. Seasonal average NO mixing ratios on the W-E Sierra Nevada transect and White Mountains elevational transect in 2012 and 2013.

19.31 ppm h which is clearly above the >3.00 ppm-h threshold indicating negative effects on above-ground biomass of semi-natural and natural vegetation dominated by annuals (CLRTAP, 2017). Much more conservative W126 index of 17.00 ppm h set as sufficient to protect vegetation from ozone exposures (US Federal Register, 2015) was exceeded at FL and PR (17.21 and 23.28 ppm h, respectively), while no exceedances were determined for HL (13.81 ppm h), and WB (14.65 ppm h). At the WMS sites, the SUM0 values ranged between 32.39 and 70.54 ppm h. The AOT40 values exceeded 3.00 ppm h in all measured sites and were between 5.42 and 23.89 ppm h. The W126 threshold of 17 ppm h was exceeded at BRS in 2012 (18.32 ppm h), and WMS in both years (26.50 and 19.53 ppm h in 2012 and 2013,

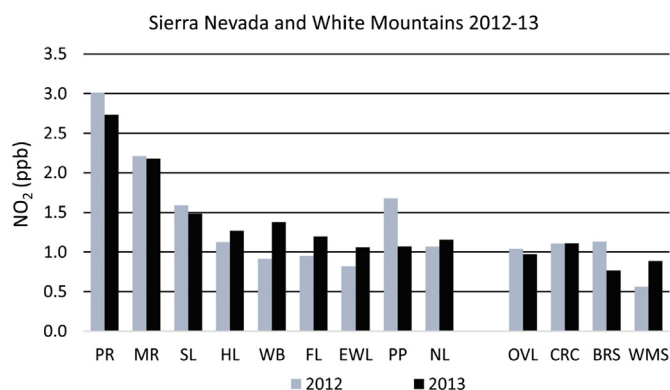


Fig. 4. Seasonal average NO_2 mixing ratios on the W-E Sierra Nevada transect and White Mountains elevational transect in 2012 and 2013.

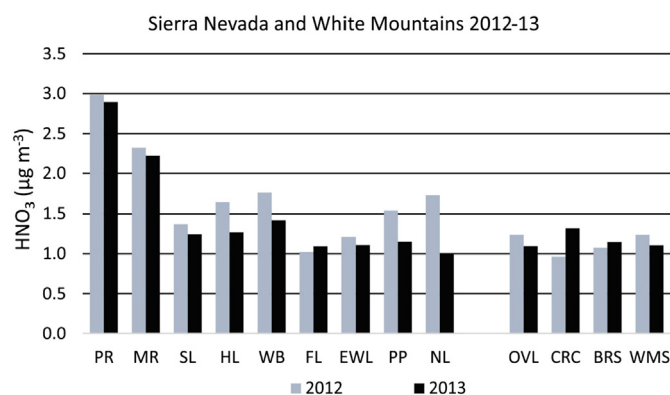


Fig. 5. Seasonal average HNO_3 concentrations on the W-E Sierra Nevada transect and White Mountains elevational transect in 2012 and 2013.

respectively). Other sites had values below the phytotoxicity threshold: OVL (2013) – 3.68 ppm h; BRS (2013) – 11.94 ppm h, and CRC-R (2013) – 5.84 ppm h (Table A-2).

3.3. Total inorganic gaseous N

In SNM seasonal average concentrations of total inorganic gaseous N, consisting of the sum of four nitrogenous pollutants, were highest at PR reaching $10.2 \mu\text{g N m}^{-3}$ in 2012 and $9.5 \mu\text{g N m}^{-3}$ in 2013. These values were slightly lower at MR ($8.1 \mu\text{g N m}^{-3}$ in 2012, and $8.4 \mu\text{g N m}^{-3}$ in 2013), while much lower values, ranging from 4.0 to $6.3 \mu\text{g N m}^{-3}$, were determined on the rest of the transect during both seasons. Ammonia was the greatest contributor to gaseous N_r on the entire transect, followed by NO, NO_2 , and HNO_3 . Values of total inorganic gaseous N in WM were similar to those determined at the remote and high elevation SNM sites, and stayed below $4.4 \mu\text{g N m}^{-3}$ in 2012, and $6.2 \mu\text{g N m}^{-3}$ in 2013. Also similar to the SNM sites, NO and NH_3 were the dominant components of N gaseous pollutants. There was no clear evidence of an effect of elevation on total N_r inorganic gaseous pollutants in WM (Fig. 6, Table A-3).

3.4. Ratio of reduced/oxidized N gases

The ratio of reduced (NH_3)/oxidized (NO, NO_2 , and HNO_3) forms of gaseous N_r pollutants in SNM gradually decreased with increasing distance from CVC: from 1.9 (2012) and 2.0 (2013) at PR, to 0.7 (2012) and 0.8 (2013) at NL, the site furthest east of CVC. The reduced/oxidized N_r ratios were higher in 2013 than in 2012 at all monitoring sites, averaging 42% higher in 2013 (Fig. 7, Table A-3). In WM these ratios were generally lower in 2012 (≤ 0.8) than in 2013 (≤ 1.0), with the exception of WMS having similar values (0.50 and 0.6) in both years. The OVL values in both years were similar to those at NL on the east end of the SNM transect. In 2012, the ratio at CRC was the lowest among all monitored sites (0.3). In 2013, the CRC and BRS ratios were similar to those at OVL and NL (Fig. 7, Table A-3).

4. Discussion

4.1. Levels and distribution

4.1.1. Ammonia

Highly elevated NH_3 concentrations were observed on the western end on the SNM transect at PR with the summer season averages of $7.8 \mu\text{g m}^{-3}$ in 2012 and $7.5 \mu\text{g m}^{-3}$ in 2013 (Tables 3 and 4). These concentrations are similar to 7.3 in 2012 and $8.8 \mu\text{g m}^{-3}$ in 2013 measured at Ash Mountain in Sequoia & Kings Canyon National Park (AMoN, 2018), but higher than $4.5 \mu\text{g m}^{-3}$ measured at the same site in 1999 (Bytnerowicz et al., 2002) and $5.2 \mu\text{g m}^{-3}$ determined at the western

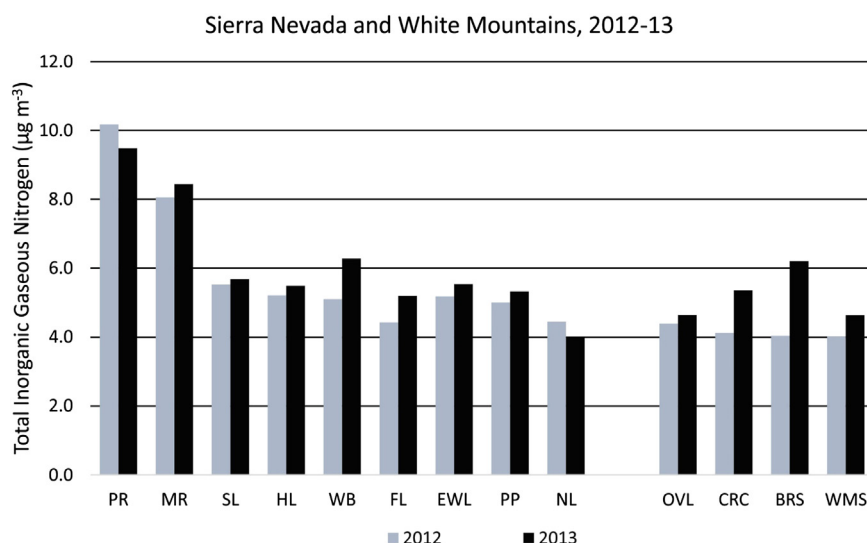


Fig. 6. Seasonal average inorganic gaseous N on the W-E Sierra Nevada transect and White Mountains elevational transect in 2012 and 2013.

end of the San Joaquin River transect in 2002 (Cisneros et al., 2010). However, these values were lower than 10.0 to 13.6 $\mu\text{g m}^{-3}$ measured with passive samplers on the southwestern slopes of SNM in 2007 (Bytnerowicz et al., 2016). During airborne observations of the CalNex campaign, NH_3 concentrations over CVC were $\sim 5.6 \mu\text{g m}^{-3}$ in June 2010 (Schiferl et al., 2014). In general, our data and results of other studies in SNM (Table 5) indicate that NH_3 concentrations in CVC and western SNM slopes are substantially elevated and at levels similar or higher to those in the most NH_3 -polluted regions of the United States (Plautz, 2018).

Remote and higher elevation sites of the SNM transect east of MR had significantly lower values: $\leq 3.5 \mu\text{g m}^{-3}$ in 2012 and $\leq 4.2 \mu\text{g m}^{-3}$ in 2013 (Tables 3 and 4, Fig. 2) with the exception of WB in 2013. These values are similar to those determined in the Lake Tahoe Basin (Table 5). These significantly reduced values indicate a rapid deposition of NH_3 to the landscape due to its high deposition velocity (Zhang et al., 2003), and its dilution with increasing distance from CVC. There is a high probability that the Aspen Fire burning just north of the SNM

transect (Burley et al., 2016) resulted in increased ambient concentrations of NH_3 , total reactive N, and $\text{N}_{\text{reduced}}/\text{N}_{\text{oxidized}}$ values in summer 2013. This could especially be the case for WB located closest to the fire. Ammonia concentrations at high elevation sites of the WM transect were similar or slightly lower ($\leq 2.3 \mu\text{g m}^{-3}$ in 2012, and $\leq 3.3 \mu\text{g m}^{-3}$ in 2013; Tables 3 and 4) in comparison to the SNM sites. High NH_3 concentrations in SNM and WM, even in the most remote areas, confirm a strong regional influence of agricultural NH_3 emissions in CVC on ambient air quality (Schiferl et al., 2014). Our results clearly indicate that NH_3 emissions in CVC cause a strong and widespread regional increase in ambient levels of this pollutant, including at remote high elevation mountain areas. Concentrations of NH_3 ($0.9\text{--}3.0 \mu\text{g m}^{-3}$) measured in the Lake Tahoe area in the northern SNM were lower than these determined in this study (Table 5), indicating that emissions in the northern portion of CVC had lower impacts on SNM than those in its southern part. The 2002–2006 summer NH_3 averages in the San Bernardino Mountains east of the Los Angeles Basin were also elevated at 2.9 to $5.2 \mu\text{g m}^{-3}$ (Bytnerowicz et al., 2015). The lowest concentrations in

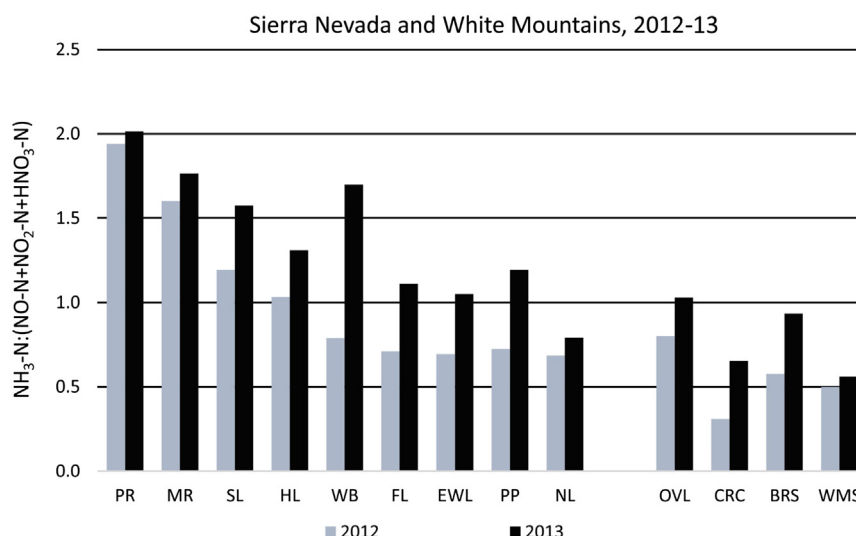


Fig. 7. Seasonal average ratios of reduced/oxidized gaseous N on the W-E Sierra Nevada transect and White Mountains elevational transect in 2012 and 2013.

Table 5

Summer season ambient nitrogenous pollutant concentrations or mixing ratios on the 2012–2013 Sierra Nevada and White Mountains transects compared with other Sierra Nevada Mountains locations.

Pollutant	Area or location & year	Concentration or mixing ratio	Reference
NH ₃ (μg m ⁻³)	SNM transect, 2012 and 2013	2.1–7.8 and 2.2–7.5	This study
	WM transect, 2012 and 2013	1.2–2.5 and 2.4–3.3	This study
	Shirley Meadow, 1989 and 1990	1.9 and 2.1	Bytnerowicz and Miller, 1991
	Whitaker Forest, 1990	1.6	Bytnerowicz and Reichers, 1995
	Sequoia NP, transect, 1999	1.6–4.5	Bytnerowicz et al., 2002
	San Joaquin River transect, 2002	2.6–5.2	Cisneros et al., 2010
	Southern SNM, 2007	2.2–13.6	Bytnerowicz et al., 2016
	Lake Tahoe Basin area, 2010	0.9–3.0	Bytnerowicz et al., 2013
	Sequoia NP, Ash Mountain, 2012–2013	7.9 and 8.6	AMoN
	Yosemite NP, Turtleback, 2012–2013	2.4 and 2.3	AMoN
	Devils Postpile National Monument, 2013	2.5	Burley et al., 2016
NO (ppb)	SNM transect, 2012 and 2013	2.1–3.4 and 2.0–3.3	This study
	WM transect, 2012 and 2013	2.3–4.0 and 2.3–4.1	This study
	Lake Tahoe Basin area, 2010	1.1–3.9	Bytnerowicz et al., 2013
	Devils Postpile National Monument, 2013	3.7	Burley et al., 2016
NO ₂ (ppb)	SNM transect, 2012 and 2013	0.8–3.0 and 1.1–2.7	This study
	WM transect, 2012 and 2013	0.6–1.1 and 0.8–1.1	This study
	Lake Tahoe Basin area, 2010	0.6–4.4	Bytnerowicz et al., 2013
	Devils Postpile National Monument, 2013	1.4	Burley et al., 2016
HNO ₃ (μg m ⁻³)	SNM transect, 2012 and 2013	1.0–3.0 and 1.0–2.9	This study
	WM transect, 2012 and 2013	1.0–1.2 and 1.1–1.3	This study
	Eastern Brook Lakes, 1987	0.4	Miller and Walsh, 1991
	Yosemite NP, 1989	0.65	Ashbaugh et al., 1991
	Shirley Meadow, 1989 and 1990	1.3 and 1.8	Bytnerowicz and Miller, 1991
	Whitaker Forest, 1990	1.0	Bytnerowicz and Reichers, 1995
	San Joaquin River transect, 2002	1.5–3.8	Cisneros et al., 2010
	Lake Tahoe Basin area, 2002	0.5–1.9	Gertler et al., 2006
	Southern SNM, 2007	0.8–3.9	Bytnerowicz et al., 2016
	Lake Tahoe Basin area, 2010	0.7–2.8	Bytnerowicz et al., 2013
	Devils Postpile National Monuments, 2013	1.3	Burley et al., 2016

the western United States determined in the EPA passive sampler AMoN network in 2012 and 2013 were: Mount Rainier NP in Washington (0.3 and 0.5 μg m⁻³); Rocky Mountain NP in Colorado (0.6 and 0.7 μg m⁻³); and Brooklyn Lake in Wyoming (0.7 and 0.7 μg m⁻³). Similarly low values were also determined in Fernberg, Minnesota (0.5 and 0.6 μg m⁻³) and Hubbard Brook, New Hampshire (0.5 and 0.4 μg m⁻³) (AMoN, <http://nadp.slh.wisc.edu/amon/>). Summertime average NH₃ values in remote areas of northeastern Alberta, Canada were 0.5–0.6 μg m⁻³ in 2005–2008 (Bytnerowicz et al., 2016). The above comparisons clearly show that even the lowest NH₃ levels in California mountains are elevated compared to the North American continental summer-time background concentrations of 0.3–0.7 μg m⁻³.

In order to look at our data in a broader temporal context, we estimated the ratios of NH₃ concentrations in summer to annual concentrations based on 2012 and 2013 data at the Ash Mountain site in Sequoia & Kings Canyon National Park and at the Turtleback Dome site in Yosemite National Park. Ratios of summer:annual concentrations were highly similar at both sites and years, ranging from 1.7–1.9 (Table A-4), suggesting that summertime NH₃ concentrations are nearly double the annual average concentrations.

4.1.2. Nitric oxide and nitrogen dioxide

Mixing ratios of both NO and NO₂ on the SNM and WM transects were similar to other studies in SNM (Table 5). No significant trends in NO concentrations related to distance from the CVC pollution source area and increasing elevation were observed. Mixing ratios for NO₂ were significantly higher at PR and MR than at sites >20 km east of the pollution source area and >1500 m elevation (Fig. 4; Tables 3 and 4). The lowest mixing ratios determined in both mountain ranges (<1 ppb) could be considered as the regional background of NO₂. In general, NO and NO₂ values on the SNM and WM transects as well as in other SNM sites (Table 5) are within ranges typical for rural areas in North America of 0.2–10 ppb (Seinfeld and Pandis, 1998).

4.1.3. Nitric acid

Nitric acid spatial distribution in SNM resembled that for NH₃ and NO₂ described above – beyond a distance >20 km from CVC and >1500 m elevation, HNO₃ concentrations were between 1.0 and 1.8 μg m⁻³, which are about 2-fold lower than those at PR and MR. Nitric acid concentrations on the WM transect were similar to those at the high elevational SNM sites, and did not show any clear distributional trend (Tables 3 and 4; Fig. 5). Concentrations of HNO₃ on both transects were similar to other SNM studies, however the lowest seasonal concentrations on both transects (1.0 μg m⁻³ in SNM and WM) were higher than 0.8 μg m⁻³ measured in eastern SNM near Mammoth Lakes, or 0.5–0.7 μg m⁻³ at the least polluted sites in the Lake Tahoe area (Table 5). For a comparison, the lowest HNO₃ concentrations in the San Bernardino Mountains of southern California in 2002–2006 were quite variable between individual years ranging from 0.2 to 1.2 μg m⁻³ (Bytnerowicz et al., 2015). In northeastern Alberta, Canada, the lowest summer season HNO₃ values were 0.2–0.6 μg m⁻³ (Bytnerowicz et al., 2010, 2016). These comparisons show that the regional background established at high central SNM sites was higher than in northern SNM and other areas in North America. Our results indicate a strong impact of photochemical smog from the CVC on the surrounding areas, even as distant and high in elevation as the WM transect.

As noted above for NH₃, we estimated the ratios of HNO₃ concentrations in summer to annual concentrations based on 2012 and 2013 data at the Ash Mountain site in Sequoia & Kings Canyon National Park and at the Turtleback Dome site in Yosemite National Park. Ratios of summer:annual concentrations were highly similar at both sites and years, ranging from 1.6 to 1.8 (Table A-4), suggesting that summertime HNO₃ concentrations are nearly double the annual average concentrations.

4.1.4. Total N and N_{reduced}/N_{oxidized}

Concentrations of total N inorganic gases on the western portion of the SNM transect at PR (~10 μg N m⁻³) and MR (~8 μg N m⁻³) in

both years were much higher than those at the remote SNM and WM sites ($\sim 4\text{--}6\ \mu\text{g N m}^{-3}$) (Table A-3). This is a clear indication of potentially elevated N deposition caused by these gases which was confirmed by the CMAQ model N deposition values (Table 1). Therefore much higher ecological effects can be expected in forests near CVC. The PR and MR sites had also much higher $N_{\text{reduced}}/N_{\text{oxidized}}$ values. In 2012, at PR that ratio was ~ 1.9 and at MR ~ 1.6 , both values much higher than 1.2 at SL, 1.0 at HL, 0.7–0.8 at the remaining SNM sites, and 0.3–0.6 at the high elevation WM sites. In 2013, these ratios were much higher at the remote SNM sites and WM sites most likely due to the NH_3 emissions from the nearby wildland fires, especially the Aspen Fire. That was especially evident at WB that reached 1.7 in 2013 compared to 0.8 determined for that site in 2012 (Table A-3).

4.1.5. Ozone

While spatial trends of seasonal O_3 mixing ratios on the SNM transect determined with passive samplers are inconclusive, the real-time data provided by active monitors indicate strong impacts of photochemical smog generated in CVC on the western SNM. Results of the real-time O_3 measurements for the western portion of the SNM transect show occasional values exceeding 90 ppb set as the 1-h California Ambient Air Quality Standard (CAAQS). An extremely high value of 186.8 ppb at SL in 2013 could be related to the nearby Aspen Fire. Smoke containing VOCs and NO_x drained and pooled in the Shaver Lake area which could result in formation of high O_3 mixing ratios. Between the PR - FL portion of the SNM transect, strong diurnal fluctuations occurred in all sites, with those close to CVC characterized by low nighttime values and elevated daytime maxima (Fig. A-5). Such distribution of O_3 mixing ratios is typical for locations affected by the nearby photochemical smog source areas (Lu and Turco, 1996). Strongly pronounced differences between elevated daytime O_3 and low nighttime values were recorded in Sequoia & Kings Canyon NP downwind of CVC (Bytnerowicz et al., 2002) and the San Bernardino Mountains downwind of the Los Angeles Basin (Bytnerowicz et al., 2007). Low O_3 levels at night are caused by a lack of photochemical reactions, titration of O_3 by NO emitted from combustion engines, and dry deposition of O_3 (Seinfeld and Pandis, 1998).

A clear increase of the seasonal O_3 mixing ratios with elevation on the WM transect (Fig. A-4) is consistent with other reports from high elevation areas (Burley et al., 2015, 2016). As expected, the measured O_3 mixing ratios increase with elevation because of increasing proximity to the stratospheric O_3 layer and greater impacts from stratospheric intrusions. Since these sites are not influenced by local emissions of O_3 precursors, their 50–60 ppb range represents the “polluted free tropospheric background” for O_3 along the eastern boundary of California. The O_3 mixing ratios measured in the White Mountains are very similar to the levels measured in background free tropospheric air arriving at elevations between 2500 and 4500 m along the western coast of the contiguous United States (Jaffe et al., 2018).

All WM sites (Fig. A-6) were characterized by flat diurnal curves similar to those determined there in 2009 (Burley and Bytnerowicz, 2011). However, the absolute O_3 values determined in this study were about 5–6 ppb higher for the BRS site, and about 10 ppb higher for the WMS site, compared to the values measured in 2009. This could be an indication of the recently observed increase in the background O_3 in the western US, which has been attributed to an increasing influence of long-range transport of polluted air masses, including those from SE Asia (Cooper et al., 2011), as well as higher emissions of VOCs and NO_x (O_3 precursors) from wildland fires that are increasing in size and number in the Western U.S. (Jaffe et al., 2013). The observed differences could also reflect (i) the slightly different measurement locations used in 2009 vs. 2012/2013; (ii) small differences in the day ranges used to calculate the diurnal plots; (iii) normal year-to-year variability in the data; and (iv) the experimental uncertainty – usually no more than ± 3 or 4 ppb – that we have routinely observed with 2B Technologies monitors deployed at remote sites.

Similar daytime and nighttime O_3 mixing ratios in WM are characteristic of high-elevation remote locations without the direct influence of pollution source areas, and where long-range transport of O_3 dominates. In such locations scavenging of O_3 by NO emissions does not take place (Musselman and Korfmacher, 2014). Our results confirm earlier findings that in complex mountain terrain diurnal O_3 profiles are highly variable and difficult to model (Burley et al., 2015). Therefore real-time measurements using active monitors are essential for understanding temporal changes among various locations. Without such an understanding, prediction of potential risks to human and ecosystem health is impossible. While short-term (week to a month) and seasonal average O_3 concentration data can be relatively easily obtained with passive samplers, such results can only serve as an initial approximate evaluation of spatial distribution of O_3 in mountainous areas (Frączek et al., 2003).

4.2. Potential ecological impacts

4.2.1. Ozone effects

The O_3 indices calculated for the sites where real-time data was available (Table A-2) showed a high potential for O_3 phytotoxic effects. The AOT40 threshold for negative impacts on the above-ground biomass of semi-natural and natural vegetation dominated by annual plants, which is set at 3 ppm h (CLRTAP, 2017), was exceeded several fold in most of the sites. That indicates that the health of individual species and the composition of plant communities are at risk in the areas near all the monitoring sites in SNM and WM. Much more conservative W126 values of 17 ppm h, set to protect vegetation from ozone exposures (US Federal Register, 2015), was exceeded on the west end of the SNM transect and high elevation sites in WM. Negative effects of O_3 on forest trees of the western SNM recorded in the 1970s and 1980s (Miller and Millecan, 1971; Panek et al., 2013) are most likely still occurring. However, in recent decades no wide-scale surveys of O_3 injury to forest trees in SNM have been conducted to confirm this statement.

4.2.2. Effects of N pollutants and N deposition

At the levels of NH_3 , NO , NO_2 , and HNO_3 measured on the SNM and WM transects as two-week averages, no direct phytotoxic effects caused by these pollutants are expected (Bytnerowicz et al., 1998), although NH_3 concentrations are likely sufficient to affect sensitive lichen communities in some of the transect sites (Cape et al., 2009). However, in considering the potential for overall effects to terrestrial and aquatic ecosystems in the SNM and WM, it would be beneficial to focus future research on the impacts of elevated ambient O_3 and N_x deposition.

Amounts of N deposited to California ecosystems are among the highest in the US, often exceeding critical loads (CL) of N deposition. This results in impacts on forests and other ecosystems downwind of major pollution source areas such as the Los Angeles Basin or CVC (Fenn et al., 2010; Bytnerowicz et al., 2015; Almaraz et al., 2018). However, N deposition and exposure varies greatly across the landscape. In this study, NH_3 concentrations, with summertime average values ranging from $2.1\text{--}7.8\ \mu\text{g m}^{-3}$ in SNM and $1.2\text{--}3.3\ \mu\text{g m}^{-3}$ in WM, likely impact sensitive lichen species in the more westerly sites. The proposed critical level for atmospheric NH_3 for impacts to epiphytic lichen communities is $1\ \mu\text{g m}^{-3}$, as an annual average concentration (Cape et al., 2009). Based on ratios of NH_3 concentrations in summer versus annual average concentrations at analogous sites in Yosemite and Sequoia & Kings Canyon National Parks we estimated the annual average concentrations of NH_3 at our SNM study sites. The annual average NH_3 concentrations ranged from 1.1 to $4.4\ \mu\text{g m}^{-3}$ in SNM in both years. Based on these estimated NH_3 concentrations we expect epiphytic lichen communities to be affected by NH_3 at all of the SNM sites. Most of the WM sites are above tree line and we do not have critical level information for rock-inhabiting lichens.

Furthermore, estimated annual N deposition at the study sites from the CMAQ model (Table 1) also confirm that the more polluted forest sites in this study exceed the N deposition CL of 3–5 kg N ha⁻¹ yr⁻¹ for epiphytic lichen communities (Fenn et al., 2010, 2008). This would include the PR, MR, and SL sites where annual N deposition ranges from 4.2 to 5.2 kg ha⁻¹. For the remaining six SNM sites, N deposition was approximately 3 kg ha⁻¹ yr⁻¹, which is near the lower end of the CL range for effects on epiphytic lichens. However, even below the previously established N deposition CL (Fenn et al., 2010, 2008), lichen communities are being affected in California (Sarah Jovan, personal communication). More importantly, CMAQ has been shown to greatly underestimate N deposition in the regions of the Sierra Nevada Mountains that are exposed to air pollution (Fenn et al., 2010), suggesting that other sites exceed the lichen CL as also discussed above in relation to the epiphytic lichen NH₃ critical level. In this study we estimated annual dry deposition at PR, SL, and PP with the inferential approach (Table A-5), and this yielded dry deposition estimates that were 1.6–3.4 times higher than CMAQ dry deposition. As verification that our inferential estimates are reasonable, we estimated total N deposition at SL by summing our inferential dry deposition estimate with CMAQ wet deposition to obtain a total N deposition estimate of 6.4 kg ha⁻¹ yr⁻¹ (Table 1 and A-5). This is very similar to throughfall N deposition of 5.7 kg ha⁻¹ yr⁻¹ at that site reported by Fenn et al. (2008) which is known to be a lower bound estimate of total N deposition due to canopy retention of atmospheric N (Fenn et al., 2018). A key point here is that our estimation of ecological effects across the transects in this study are conservative in nature because of the tendency of CMAQ to significantly underestimate N deposition in the SNM (Fenn et al., 2010).

Currently-used simulation models such as CMAQ typically provide deposition estimates at a 12 × 12 km grid scale. Such simulated deposition estimates are highly useful because they provide broad-scale spatial coverage in areas where measurements are not available, they include a wide array of N compounds including organic N pollutants, and deposition estimates are generally available for multiple years (Fenn et al., 2018). However, these simulated estimates also have limitations that are sometimes not acknowledged because of inadequate emissions inventories used as model input, variable land cover within each grid, incomplete understanding of atmospheric chemical reactions and limited simulation of orographic effects and cloud water deposition (Fenn et al., 2009). Models of such coarse resolution are also not effective in detecting deposition hotspots. For these reasons, model validation with empirical measurements is recommended.

Little is known of the deposition loads at which ecological endpoints such as vegetation communities and rock-inhabiting lichen communities are affected by N deposition in the higher elevation sites above the tree-line. For comparison, at a subalpine site in the Rocky Mountains in Colorado the estimated critical load for vegetation community change was between 1.9 and 3.5 kg N ha⁻¹ yr⁻¹ (McDonnell et al., 2014). CMAQ estimates of N deposition in the higher elevation transect sites above the tree-line (above ca. 2900 m) on the SNM and WM gradients ranged from 2.5–3.1 kg N ha⁻¹ yr⁻¹ (Table 1) which is within the CL range for vegetation community change in the Rocky Mountains.

High elevation SNM lakes also have relatively low (2.0 kg N ha⁻¹ yr⁻¹) CLs for eutrophication and acidification effects (Baron et al., 2011). Shaw et al. (2014) estimated a CL for acidification effects to lakes in granitic catchments in the SNM of 2.1 kg N ha⁻¹ yr⁻¹. Heard and Sickman (2016) reported that 21–37% of the high elevation lakes in Yosemite and Sequoia & Kings Canyon National Parks in SNM exceed the nitrate threshold for eutrophication effects to phytoplankton communities. Saros et al. (2011) reported a wet-deposition CL of 1.4 kg N ha⁻¹ yr⁻¹ for changes to diatom communities in two lakes in the eastern SNM in the Inyo National Forest. The more sensitive lakes and the ones likely to exceed nitrate concentration thresholds, are these located at higher elevations closer to the SNM crest and in watersheds that have minimal vegetation and are north-facing with steep slopes

(Heard and Sickman, 2016). All of the high elevation sites in our SNM and WM transects (deposition ranging from 2.5–3.1 kg ha⁻¹ yr⁻¹) are in exceedance of these critical loads for eutrophication and acidification effects to lakes.

5. Conclusions

- Elevated NH₃ concentrations and high N_{reduced}/N_{oxidized} ratios in the western portion of the SNM transect indicate strong effects of emissions from agriculture in CVC on SNM.
- There was a significant decrease of NH₃, NO₂ and HNO₃ in SNM with increasing elevation and distance from CVC. Regional background values started occurring >1500 m and 20 km from CVC and were similar to those determined in WM.
- Mean seasonal mixing ratios of O₃ in SNM did not change with distance from CVC nor elevation. In WM, these ratios increased with elevation.
- While western sites on the SNM transect were characterized by highly variable diurnal O₃ profiles, those in WM did not show diurnal variability.
- Selected phytotoxic indices indicate high potential for deleterious impacts of O₃ on sensitive vegetation in SNM and WM.
- Estimated N_r deposition values in SNM and WM are indicative of impacts on lichen communities and potential nutrient enrichment and acidification of high elevation lakes.
- It would be beneficial to focus future ecological studies in SNM and WM on impacts of elevated ambient O₃ and N_r deposition on vegetation communities including O₃-sensitive forest trees.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.scitotenv.2018.11.011>.

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