

Summer-time distribution of air pollutants in Sequoia National Park, California

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“Capsule”: *Spatial and temporal distributions of ozone, nitrogenous and sulfurous air pollutants in Sequoia National Park in summer 1999 are described.*

Abstract

Concentrations of air pollutants were monitored during the May–November 1999 period on a network of forested sites in Sequoia National Park, California. Measurements were conducted with: (1) active monitors for nitric oxide (NO), nitrogen dioxide (NO₂) and ozone (O₃); (2) honeycomb denuder/filter pack systems for nitric acid vapor (HNO₃), nitrous acid vapor (HNO₂), ammonia (NH₃), sulfur dioxide (SO₂), particulate nitrate (NO₃⁻), ammonium (NH₄⁺), and sulfate (SO₄²⁻); and (3) passive samplers for O₃, HNO₃ and NO₂. Elevated concentrations of O₃ (seasonal means 41–71 ppb), HNO₃ (seasonal means 0.4–2.9 µg/m³), NH₃ (seasonal means 1.6–4.5 µg/m³), NO₃⁻ (1.1–2.0 µg/m³) and NH₄⁺ (1.0–1.9 µg/m³) were determined. Concentrations of other pollutants were low. With increasing elevation and distance from the pollution source area of O₃, NH₃ and HNO₃ concentrations decreased. Ammonia and NH₄⁺ were dominant N pollutants indicating strong influence of agricultural emissions on forests and other ecosystems of the Sequoia National Park. Published by Elsevier Science Ltd.

Keywords: Ozone; Nitrogenous pollutants; Elevation gradient; Forests; Spatial variability; Passive samplers

1. Introduction

The Sierra Nevada Mountains, California, USA, have been characterized by moderately elevated concentrations of ozone (O₃) and nitrogenous (N) air pollutants (Böhm, 1992; Bytnerowicz and Fenn, 1996; Bytnerowicz et al., 1999). In some areas, O₃ concentrations are high enough to cause visible foliar injury and reduced retention of needles of Jeffrey and ponderosa pines (Duriscoe and Stolte, 1989). These two species are the most sensitive western United States conifers to oxidant air pollution (Miller et al., 1983). Reduction of radial growth of these two species most sensitive to O₃ exposure has also been described in the western Sierra Nevada (Peterson et al., 1987, 1991). However, in the San Bernardino

Mountains of southern California, ponderosa and Jeffrey pines with severe foliar injury often do not show reduced growth (Arbaugh et al., 1999). This can be attributed to the fertilizing effects of a long-term deposition of elevated levels of nitrogenous pollutants from fossil fuel consumption and local agricultural and feed lots emissions in the Los Angeles basin. Similar effects may also be observed in the western Sierra Nevada where N deposition from agriculture and rapidly developing urban areas in Central Valley of California may increase growth of pines on nutritionally poor granitic soils (Takemoto et al., 2001). Only limited information on levels and spatial and temporal distribution of nitrogenous air pollutants in the Sierra Nevada is available.

Sequoia National Park is one of the most frequently visited places in the western United States. Serious ecological concerns have been raised due to long-term effects of air pollution originating in the San Francisco

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Bay area and rapidly developing San Joaquin Valley on biological resources of the Park. Air quality and visibility also have to be taken into account for providing and planning recreational use of federally managed lands (Winter, 1999). While the National Park Service monitors air quality, it has been mainly done for O_3 and wet deposition (Stohlgren and Parsons, 1987; Chorover et al., 1994). Very little is known about spatial and temporal distribution of other pollutants, including very important from the ecological and health perspective nitrogenous pollutants.

The objective of this study was to characterize nitrogenous, sulfurous and ozone air pollution along an elevational gradient in Sequoia National Park during the summer. Spatial and temporal distribution of pollutants, with a special emphasis on effects of elevation, was evaluated. Several monitoring techniques designed for remote locations have been used for this purpose.

2. Methodology

2.1. Research area

Nine air pollution monitoring sites were established on the western slope of Sierra Nevada in Sequoia National Park, California (Fig. 1). All locations were

well exposed to air masses moving from the San Joaquin Valley into the western Sierra Nevada. Six monitoring sites, Ash Mountain—504 m; Three Pole Corner (also called Deer Ridge)—1222 m; Crystal Cave—1617 m; Lower Kaweah (also called Giant Forest Station)—1905 m; Marble Fork (near Lodgepole)—2025 m; and Wolverton—2207 m were located along the Kaweah/Marble Fork drainage. Stony Creek site (2006 m) was located north of the Kaweah/Marble Fork drainage, at a similar elevation to Marble Fork and Huckleberry Meadow, on a plateau that did not have direct airflow from the San Joaquin Valley. Little Baldy Saddle (2253 m) was located between the Stony Creek and the Kaweah/Marble Fork drainages and was directly exposed to airflow from San Joaquin Valley. Huckleberry Meadow (2026 m) was southeast of the Kaweah/Marble Fork drainage with the SE indirect airflow from San Joaquin Valley.

2.2. Air pollution monitoring

At Ash Mountain and Lower Kaweah continuous monitoring of O_3 was performed with Thermo Environmental Model 49 UV absorption instrument operated by the National Park Service Air Resources Division, and at Wolverton with a Dasibi Model 1003 AH photometer. Concentrations of nitric oxide (NO) and nitrogen dioxide (NO_2) were monitored at Lower

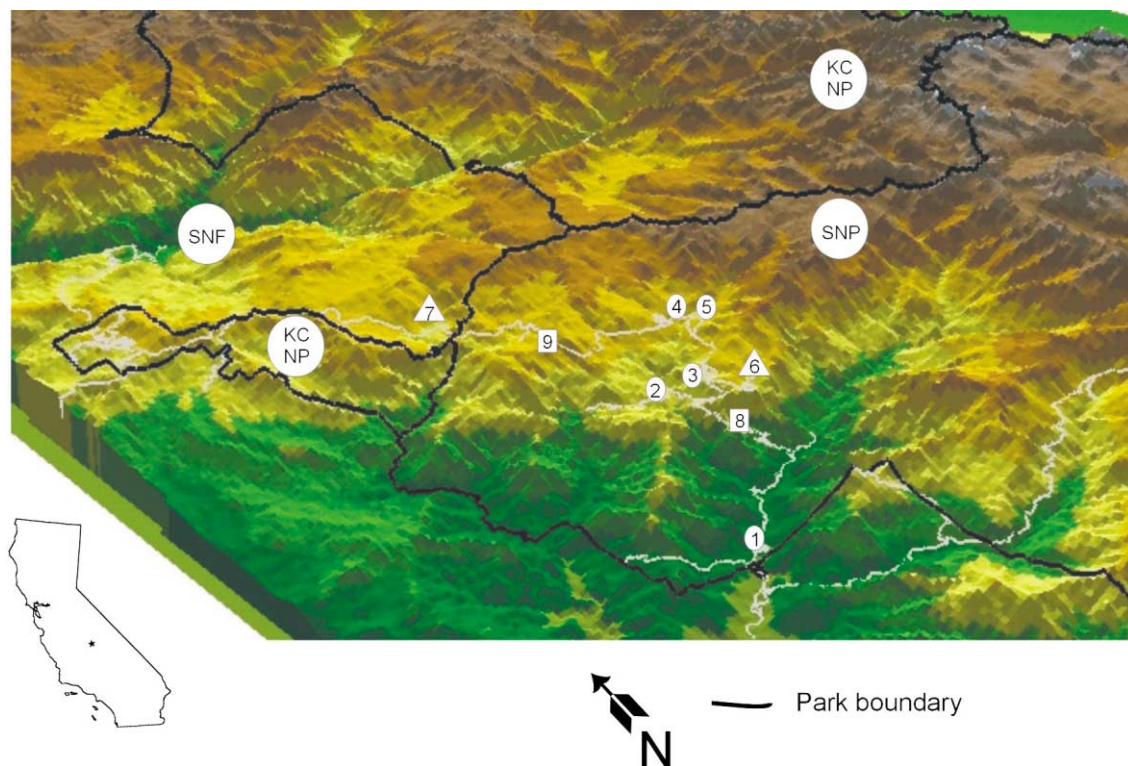


Fig. 1. Location of the monitoring plots in the Sequoia National Park, western Sierra Nevada. Circles—honeycomb denuders and complete sets of passive samplers (1) Ash Mountain, (2) Crystal Cave, (3) Lower Kaweah, (4) Marble Fork, (5) Wolverton; Triangles—complete sets of passive samplers: (6) Huckleberry Meadow, (7) Stony Creek; Squares— O_3 passive samplers. (8) Three Pole Corner, (9) Little Baldy Saddle, SNP—Sequoia National Park; KCNP—Kings Canyon National Park; SNF—Sequoia National Forest. White lines on a map show roads.

Kaweah with a Thermo Environmental Model 42 C NO/NO_x chemiluminescence instrument. The Thermo Environmental O₃ instrument was calibrated at the beginning and end of the season and checked against a calibrator every day. The Dasibi O₃ instrument was calibrated at the beginning and end of the season and checked against a calibrator every 2 weeks. All active O₃ monitors passed an independent audit performed by the California Air Resources Board. The Thermo Environmental Model 42 NO/NO₂ instrument was calibrated with NO of a known concentration and verified with an independently mixed NO standard at the beginning, middle and end of the season. Honeycomb denuder/filter pack air pollution sampler (Koutrakis et al., 1993a) were used for collection of nitric acid (HNO₃) vapor, nitrous acid (HNO₂) vapor, ammonia (NH₃), sulfur dioxide (SO₂), particulate nitrate (NO₃⁻), particulate ammonium (NH₄⁺), and particulate sulfate (SO₄²⁻) during two 24-h long periods every month (May through November 1999). Concentrations of the collected gaseous and particulate pollutants were determined with ion chromatography (HNO₃, SO₂, particulate NO₃⁻ and SO₄²⁻) and colorimetry (NH₃, HNO₂ and particulate NH₄⁺).

In addition, O₃, NO₂ and HNO₃ were monitored during 2-week long periods between mid-May and mid-October with passive samplers. Ozone was collected with Ogawa passive samplers using sodium nitrate as an absorbant (Koutrakis et al., 1993b). Nitrate resulting from oxidation of nitrate by O₃ was determined with ion chromatography (Dionex Model 4000i instrument) and concentrations of the pollutant were determined using calibration against collocated active O₃ monitors at Ash Mountain and Lower Kaweah. Nitrogen dioxide was collected with Ogawa passive samplers using triethanolamine (TEA) as an absorbant, and colorimetric determination (Beckman DU-65 Spectrophotometer) of the pollutant concentration using original manufacturer's procedure (Ogawa & Company, USA, Inc, 1998). Nitric acid vapor was collected on Nylasorb nylon filters (Nylasorb, Pall Corporation) hung under polyethylene caps protecting the filters from wind and rain. The samplers were calibrated against honeycomb denuder samplers (Bytnerowicz et al., 2002). For each location and period of collection four replicate measurements were made for O₃, three for HNO₃ and two for NO₂. During every exposure period unexposed filters were kept at room temperature as blanks for each type of passive sampler. Ozone and NO₂ concentrations from active monitors and passive samplers are expressed as ppb. For N budget calculations NO₂ concentrations from active monitors were converted to µg/m³ (1 ppb NO₂ = 1.88 µg/m³ at 25 °C, 760 mm Hg). Concentrations of gaseous and particulate N pollutants collected with honeycomb denuder/filter pack systems and HNO₃ from passive samplers were expressed µg/m³.

2.3. Statistical evaluation of data

Statistical analysis of data was performed with SigmaStat software (SPSS Science, 1997). Two-way ANOVA analysis was used to test significant differences among sites and different periods. Student's *t* test was used for comparison of performance of passive samplers against active monitors/honeycomb denuder systems. Differences are reported here as significant at *P* < 0.05.

3. Results

3.1. Active monitors

Over the entire summer season ozone concentrations at the Ash Mountain, Lower Kaweah and Wolverton monitoring sites were in the same range. Average daily concentrations at Ash Mountain and Lower Kaweah ranged between 30 and 80 ppb, while at the Wolverton site between 20 and 70 ppb. Maximum 1-h concentrations reached 120 ppb at Ash Mountain, and stayed below 110–115 ppb at the Lower Kaweah and Wolverton sites. Minimum concentrations at Ash Mountain were about 18 ppb, and at the two higher elevation sites at about 10 ppb (Fig. 2a–c). Characteristics of diurnal changes of O₃ concentrations were similar for all three sites with peak values at about 17:00 PST. Minimum concentrations were recorded at about 07:00 PST (Fig. 3a–c).

Average daily nitric oxide concentrations at Lower Kaweah were below 1 ppb during most of the season. Short-lasting daily maximum values frequently occurred and reached 24 ppb on one occasion during a prescribed burn (Fig. 4a). Average daily concentrations of NO₂ were variable and were generally below 4 ppb. Maximum daily values often exceeded 15 ppb with the highest values reaching 33 ppb (Fig. 4b). Although general characteristics of diurnal changes were similar for the entire season, differences in proportions of concentrations during different time of a day occurred for individual months. The most pronounced diurnal changes were seen in July with low nighttime values, sharp early morning increases, and highly elevated afternoon values. In October, values were higher during the afternoon and remained high during the night (Fig. 5).

3.2. Honeycomb denuder/filter pack data

Over the entire summer season the highest concentrations of HNO₃ occurred in the Ash Mountain site (seasonal mean 2.1 µg/m³). Concentrations at the higher elevation sites were significantly lower, with the lowest value of 0.6 µg/m³ determined at Wolverton (Table 1). There was a significant effect of time (*P* < 0.001) on concentrations of the pollutant. The highest concentrations

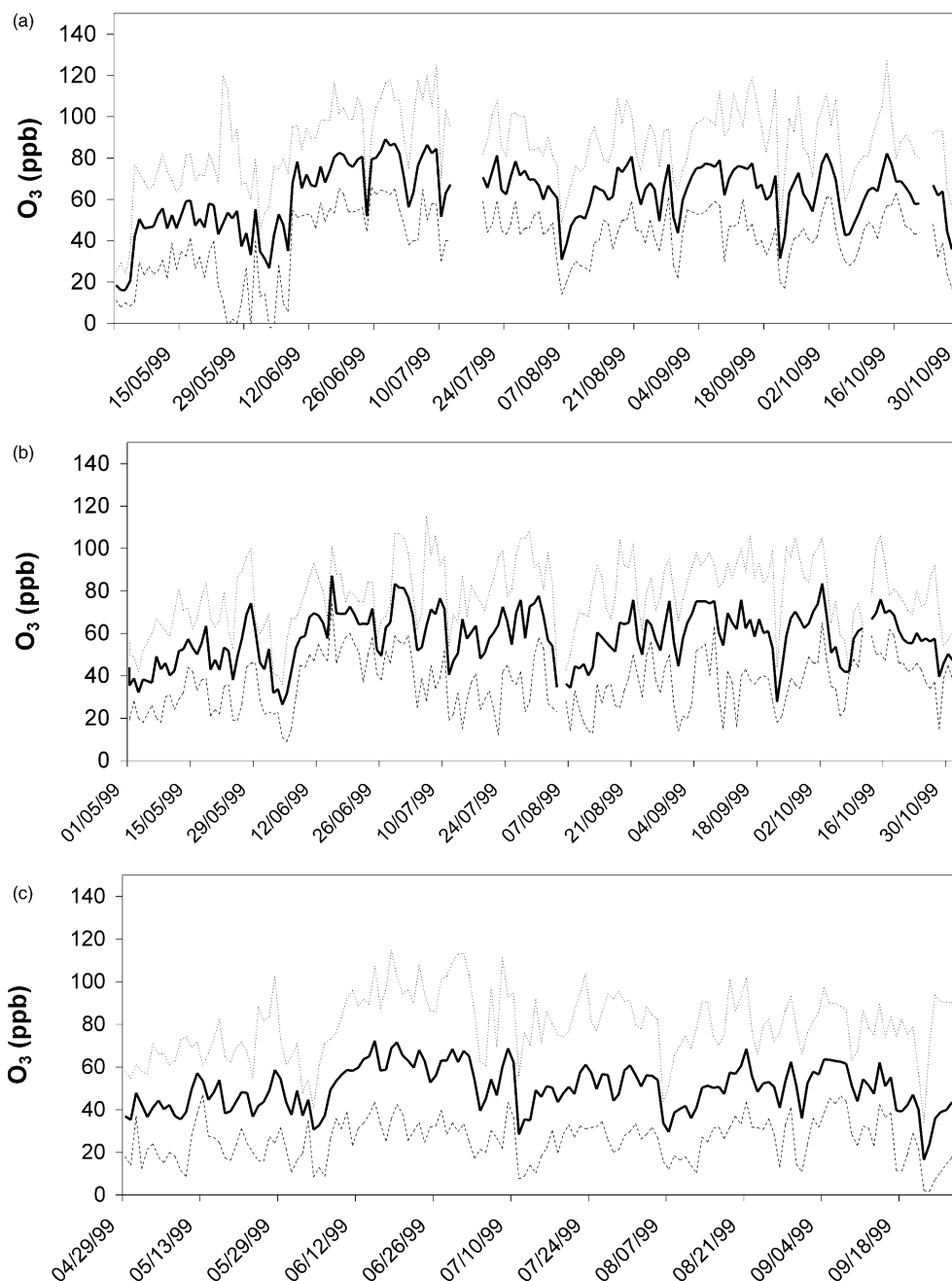


Fig. 2. Seasonal changes of daily average (solid line), maximum 1-h (dotted line) and minimum 1-h (dashed line) ozone concentrations monitored with active instruments: (a) Ash Mountain; (b) Lower Kaweah; (c) Wolverton.

were recorded during the July and August collections and the lowest in May and November (Fig. 6a).

Distribution of NH_3 concentrations was similar to those of HNO_3 . The highest levels of seasonal means were determined at Ash Mountain ($4.5 \mu\text{g}/\text{m}^3$). Other sites had significantly lower concentrations with the lowest value $1.6 \mu\text{g}/\text{m}^3$ recorded at Wolverton (Table 1). A significant effect of time ($P < 0.001$) was determined with the highest values recorded in July and August and the lowest concentrations in November (Fig. 6b).

No significant differences were determined for HNO_2 between the monitoring sites ($P = 0.108$; Table 1). However, the concentrations at Lower Kaweah in August (ranging from 2.5 to $4.1 \mu\text{g}/\text{m}^3$) were significantly higher than other values (Fig. 6c).

Concentrations of SO_2 were similar at Ash Mountain, Crystal Cave and Lower Kaweah, and significantly higher than at Marble Fork and Wolverton (Table 1). There was also a significant effect time of collection ($P < 0.001$) on SO_2 distribution. The highest values

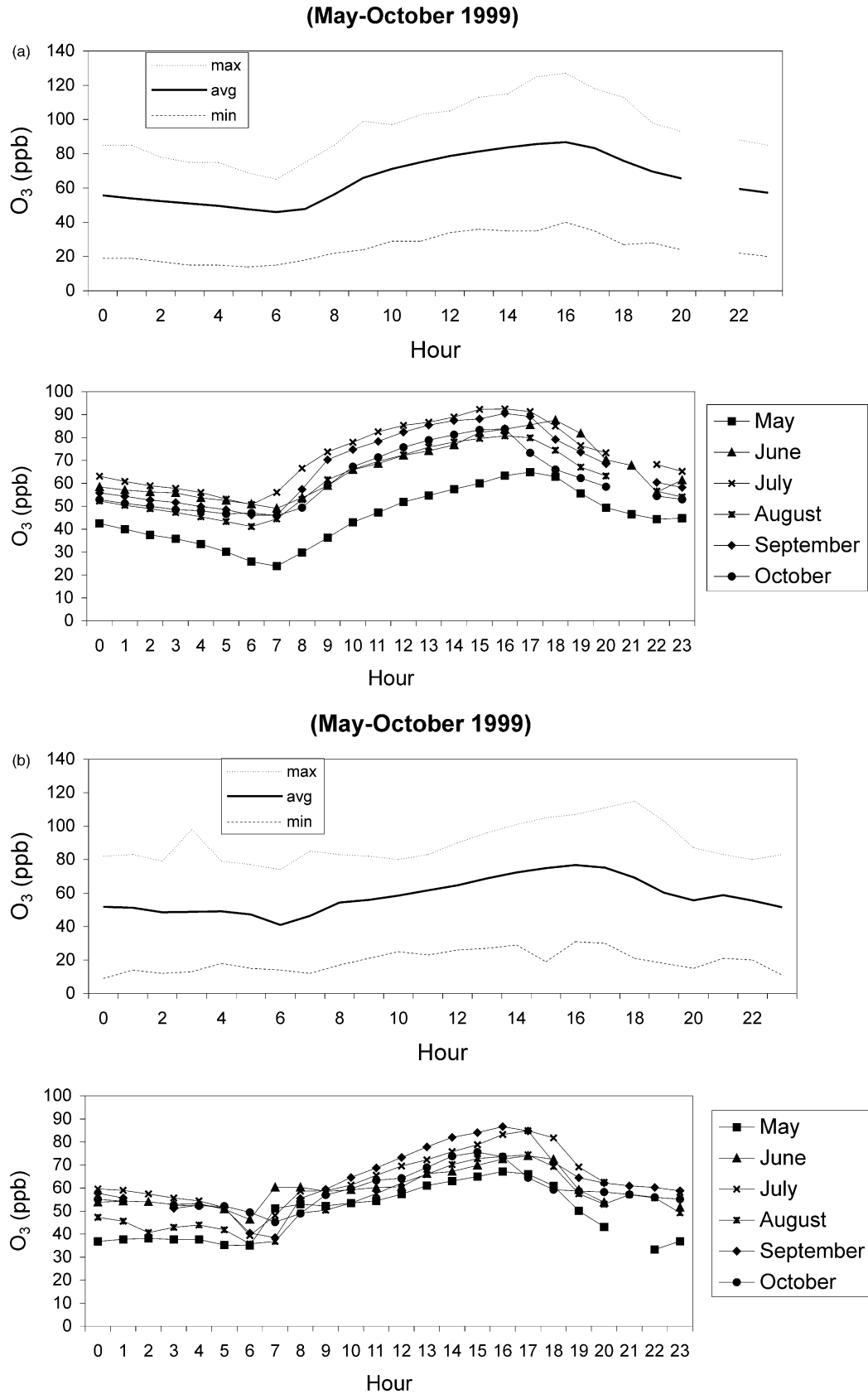


Fig. 3. Seasonal and monthly diurnal changes of ozone concentrations monitored with active instruments: (a) Ash Mountain; (b) Lower Kaweah; (c) Wolverton.

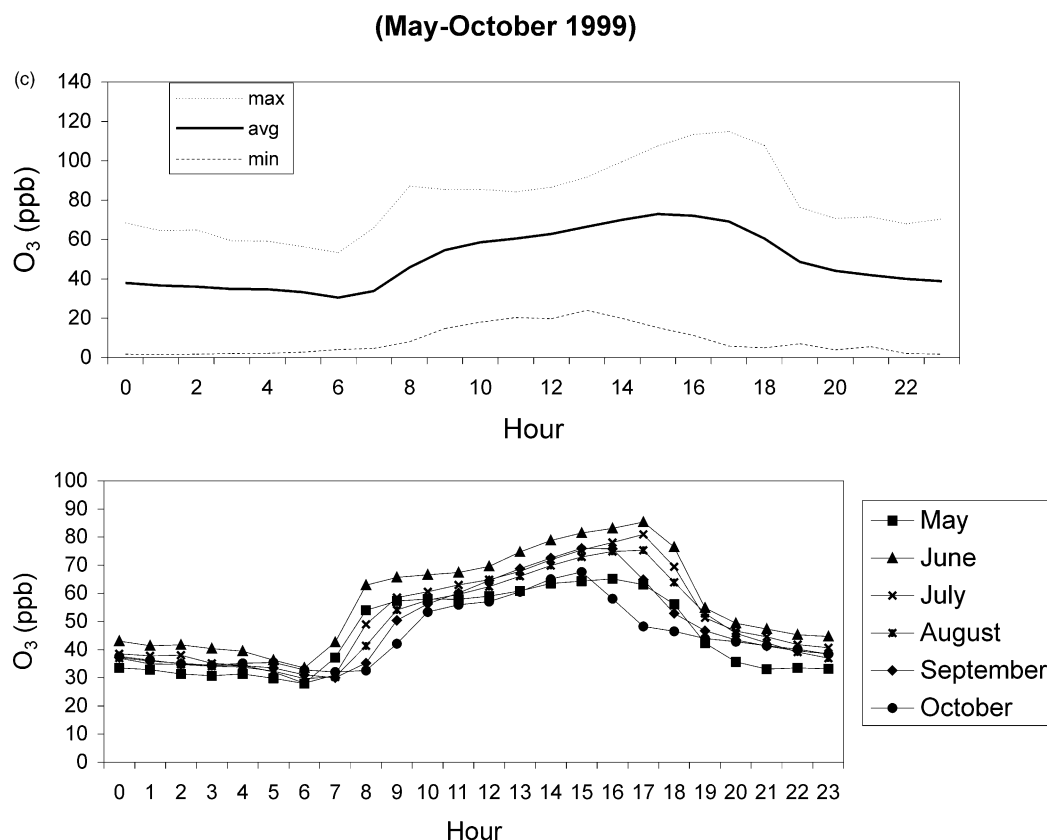


Fig. 3. (continued).

occurred in June and July reaching $3.5 \mu\text{g}/\text{m}^3$ at Ash Mountain. Concentrations were significantly lower at the end of September and remained below $0.5 \mu\text{g}/\text{m}^3$ (Fig. 6d).

The highest concentrations of particulate NO_3^- were determined at Lower Kaweah (seasonal mean $2.0 \mu\text{g}/\text{m}^3$), and the lowest levels at Wolverton (seasonal mean $1.1 \mu\text{g}/\text{m}^3$). Other sites had seasonal mean values between 1.1 and $1.3 \mu\text{g}/\text{m}^3$ that did not significantly differ from the Ash Mountain and the Wolverton concentrations (Table 1). A significant effect of time ($P < 0.001$) occurred with the highest values on 13 May (Fig. 6e).

Similarly to particulate NO_3^- , the highest levels of particulate NH_4^+ were determined at Lower Kaweah (seasonal mean $1.9 \mu\text{g}/\text{m}^3$) and the lowest at Wolverton (seasonal mean $1.0 \mu\text{g}/\text{m}^3$). Other sites had seasonal mean values between 1.3 and $1.6 \mu\text{g}/\text{m}^3$, and did not significantly differ from the Lower Kaweah and Wolverton sites (Table 1). A clear effect of time was seen with the 1–3 September concentrations significantly higher than during other periods (Fig. 6f).

No significant effects of location were seen for particulate SO_4^{2-} concentrations (Table 1). However, at the Marble Fork site on 1–3 September elevated SO_4^{2-} concentrations reaching $7.5 \mu\text{g}/\text{m}^3$ were determined. There

was a trend of much lower concentrations of particulate SO_4^{2-} after the 29–30 September collection (Fig. 6g).

3.3. Passive sampler data

Two-week long average concentrations of O_3 were consistently the highest at the Three Pole Corner site (seasonal mean 72 ppb). The Ash Mountain and Little Baldy Saddle sites were not significantly different with concentrations of 64 and 63 ppb, respectively. The lowest seasonal mean was recorded at Wolverton (41 ppb). Seasonal mean O_3 concentrations at other sites ranged between 46 and 60 ppb (Table 2). A significant effect of sampling period ($P < 0.001$) occurred with the highest concentration recorded between 9 June–3 August, and 1–14 September (Fig. 7).

The highest HNO_3 concentrations were recorded at Ash Mountain (seasonal mean $2.9 \mu\text{g}/\text{m}^3$) and the lowest at Wolverton (seasonal mean $0.4 \mu\text{g}/\text{m}^3$). Concentrations for the remaining sites ranged between 0.6 and $1.1 \mu\text{g}/\text{m}^3$ (Table 2). A significant effect of time on HNO_3 concentrations ($P < 0.001$) occurred with the highest values recorded in the middle of the season (9 June through 14 September; Fig. 8a).

Concentrations of NO_2 were the highest at the Lower Kaweah (2.0 ppb) and the Ash Mountain (1.7 ppb)

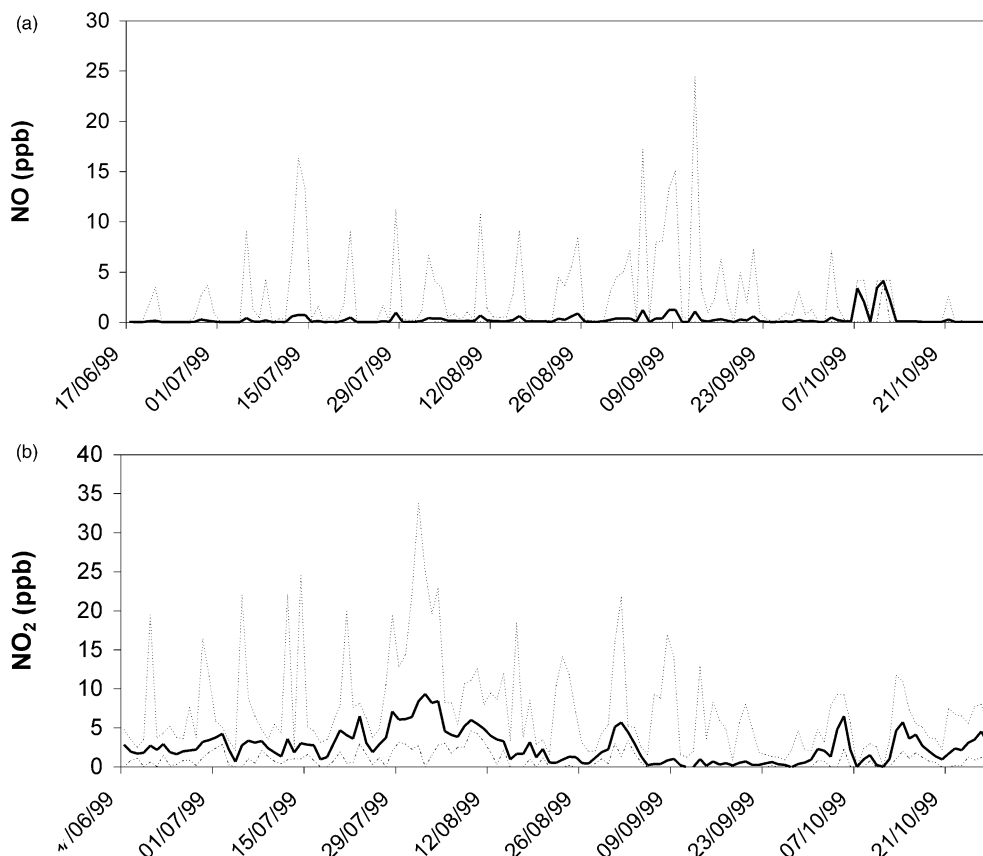


Fig. 4. Seasonal changes of daily average, maximum 1-h and minimum 1-h concentrations (a) NO and (b) NO₂ at Lower Kaweah.

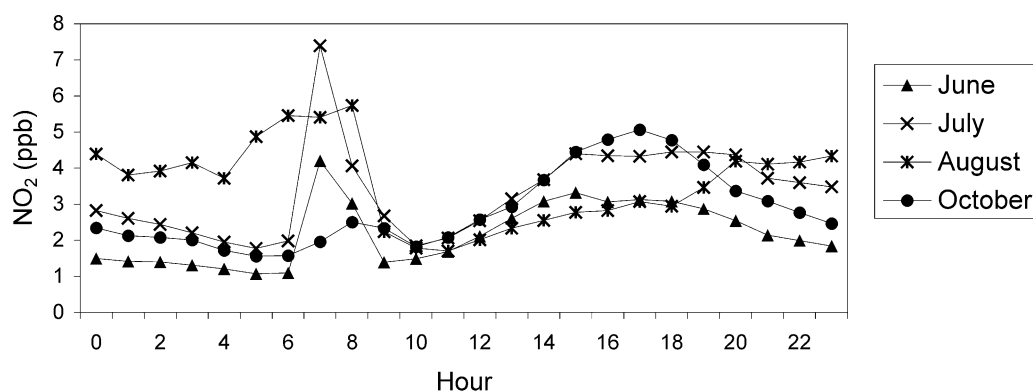


Fig. 5. Diurnal changes of NO₂ concentration measured at Lower Kaweah presented as monthly averages.

sites. The other sites had significantly lower values ranging between 1.0 and 1.3 ppb (Table 2). Significant effect of time on NO₂ levels was determined ($P=0.019$) with the highest concentrations recorded during the 21 July–3 August period and the lowest during the 14–30 September and 30 September–14 October periods (Fig. 8b).

3.4. Evaluation of passive samplers performance

Two-week long averages of O₃ concentrations from the Ogawa passive samplers and real-time concentrations

measured with active monitors at the Ash Mountain and Lower Kaweah sites were in the same range (33–77 and 40–78 ppb, respectively). At these locations no significant differences between concentrations obtained with the two methods were observed. Precision of measurements with the Ogawa O₃ passive samplers was high—relative standard deviation of four replicate measurements stayed between 0.7 and 11.0% (average 3.0%) during the monitoring period.

Ranges of HNO₃ concentrations determined with honeycomb denuder systems and passive samplers were

Table 1
Summary of honeycomb/filter pack air pollution sampler results presented as seasonal means with standard deviation (in parentheses), and ranges of concentrations ($\mu\text{g}/\text{m}^3$)^a

Location	HNO ₃	NH ₃	HNO ₂	SO ₂	NO ₃ ⁻ part.	NH ₄ ⁺ part.	SO ₄ ²⁻ part.
Ash Mountain	2.1 (1.4) a 0.1–4.6	4.5 (2.4) a 1.0–8.0	0.15 (0.15) 0–0.3	1.3 (1.1) a 0–3.5	1.3 (1.1) ab 0.3–3.7	1.3 (2.2) ab 0.1–7.5	0.6 (0.5) 0.20–1.6
Crystal Cave	0.9 (0.5) b 0.1–1.5	2.9 (1.6) b 0.3–4.6	0.2 (0.2) 0.0–0.7	0.9 (0.9) a 0–2.5	1.2 (1.1) ab 0.3–3.3	1.6 (2.8) ab 0.0–8.0	0.7 (0.4) 0.1–1.5
Lower Kaweah	0.9 (0.6) b 0.2–2.0	2.6 (1.6) bc 0.1–5.4	0.6 (1.3) 0.0–4.1	1.1 (0.7) a 0–2.7	2.0 (1.9) a 0.4–7.2	1.9 (2.5) a 0.1–7.3	0.8 (0.7) 0.2–2.1
Marble Fork	0.8 (0.5) b 0.1–1.7	2.0 (1.1) bc 0.2–3.5	0.2 (0.2) 0.0–0.6	0.6 (0.6) b 0–2.2	1.1 (0.9) ab 0.2–3.2	1.5 (2.5) ab 0.1–7.5	1.5 (2.5) 0.1–7.5
Wolverton	0.6 (0.3) b 0.2–1.0	1.6 (0.9) c 0.4–3.2	0.2 (0.1) 0.1–0.4	0.6 (0.5) b 0–1.7	1.1 (0.7) b 0.2–2.5	1.0 (1.7) b 0–5.4	0.8 (0.7) 0.0–2.1
P value	<0.001	<0.001	0.108	<0.001	0.034	0.016	0.480

^a Different letters following mean and S.D. indicate significant differences between monitoring sites at a specified “P” value.

similar (0.6–2.1 and 0.4–2.9 $\mu\text{g}/\text{m}^3$, respectively). Statistical evaluation of the HNO₃ data indicated that in four out of five sites where both honeycomb denuder systems and passive samplers were used, concentrations did not significantly differ. This suggests that these HNO₃ passive samplers could be used for estimates of ambient levels of the pollutant in remote mountain locations. However, due to different collection regimes (2 week-long integrated values for passive samplers versus two 24-h measurements per month during the growing season with honeycomb denuder systems), such a comparison has to be viewed with caution. These results also indicate that two different sampling regimes and monitoring methods provided very similar estimates of HNO₃ contamination in the study area. Precision of measurements with the HNO₃ passive samplers was good—relative standard deviation of three replicate measurements stayed between 0.8 and 25.4% (average 9.2%) during the entire monitoring period. Precision of HNO₃ passive samplers could be additionally improved if a diffusion barrier providing uniform flow of air to the collection medium is installed in the samplers.

The 2-week long averages of NO₂ concentrations at the Lower Kaweah site using Ogawa passive samplers were lower than those from the active monitor (ranges 1.3–2.8 and 0.5–5.0 ppb; mean seasonal values 2.04 and 2.62 ppb, respectively). However, no significant differences between the two methods were found. Precision of measurements with the Ogawa NO₂ passive samplers was high—the relative standard deviation of two replicate measurements ranged between zero and 28.5% (average 5.6%) during the entire monitoring period.

4. Discussion

4.1. Comparison of pollutant concentrations with other mountain locations and evaluation of their phytotoxic potential

The reported O₃ concentrations at the Sequoia National Park locations were elevated and typical for the western slopes of the Sierra Nevada. Ozone concentrations were similar to the values determined on the high elevation (1130–1980 m) network of active monitors in the western Sierra Nevada in 1992–1994, when the 24-h average seasonal O₃ concentrations in those sites ranged between 38 and 74.5 ppb (Bytnerowicz et al. 2000). In the 1980s, the growing season mean ozone concentration of about 63 ppb measured at the Ash Mountain location (Böhm, 1992) was similar to the values found in this study. Similarly, at the Lower Kaweah site, the values from this study were close to the seasonal mean of about 58 ppb measured in the 1980s (Böhm, 1992). Our values were also similar to the O₃ concentrations recorded at six remote locations on the

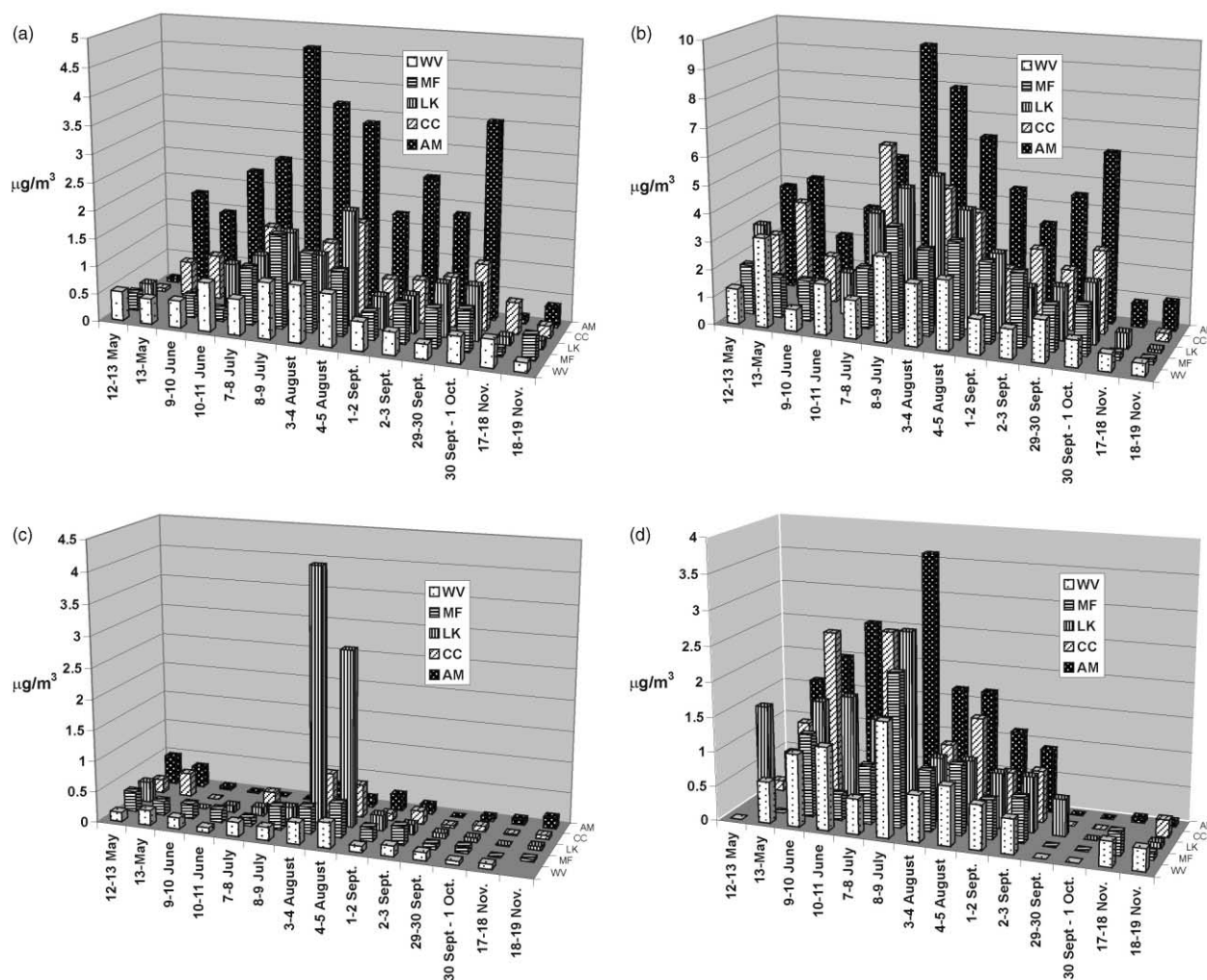


Fig. 6. Concentrations of nitrogenous and sulfurous pollutants measured with honeycomb denuder/filter pack air pollution systems expressed as $\mu\text{g}/\text{m}^3$: (a) nitric acid (HNO_3); (b) ammonia (NH_3); (c) nitrous acid (HNO_2); (d) sulfur dioxide (SO_2); (e) particulate nitrate (NO_3^-); (f) particulate ammonium (NH_4^+), and (g) particulate sulfate (SO_4^{2-}). WV—Wolverton; MF—Marble Fork; LK—Lower Kaweah; CC—Crystal Cave; AM—Ash Mountain.

western slopes of the Sierra Nevada in summer 1992 (Van Ooy and Carroll, 1995). In the Cascade Mountains in Washington, the summer season monthly mean O_3 concentrations were much lower and ranged between 19 and 35 ppb (Brace and Peterson, 1998).

Comparison of O_3 concentrations in the Sierra Nevada forest sites with similar forested sites in the San Bernardino Mountains of southern California and other locations in the Sierra Nevada may provide some perspective on potential risks to forest health. In the San Bernardino Mountains in the 1960s, the forest decline associated with O_3 injury was reported for the first time (Miller et al., 1963). At Barton Flats in the eastern San Bernardino Mountains (moderately polluted site), the summer season mean O_3 concentration was 76 ppb, with peak values reaching 200 ppb in early 1990s (Watson et al., 1999). In the highly polluted western San Bernardino Mountains where extensive forest decline has been reported (the Lake Gregory area), between

1973 and 1987, summer season mean O_3 concentrations declined from about 100 ppb to about 70 ppb, while the maximum 1-h levels dropped from 350 ppb to 230 ppb (Miller, 1992).

Seasonal mean O_3 concentrations at some of the studied sites (Three Pole Corner, Lower Kaweah, Little Baldy Saddle) were similar to those recorded in the San Bernardino Mountains. Although peak O_3 values at the Sequoia sites were below 140 ppb, extensive injury of ponderosa and Jeffrey pines in Sequoia National Park has been reported (Duriscoe and Stolte, 1989). Ponderosa pine seedlings exposed to levels of O_3 similar to those in this study, showed increased chlorotic mottle and premature senescence of needles (Takemoto et al., 1997). Risk of O_3 phytotoxic effects to pines and other species may be especially high in the beginning of a growing season, when plants are physiologically active and their stomatal conductance is high, similar to that described by Panek and Goldstein (2001).

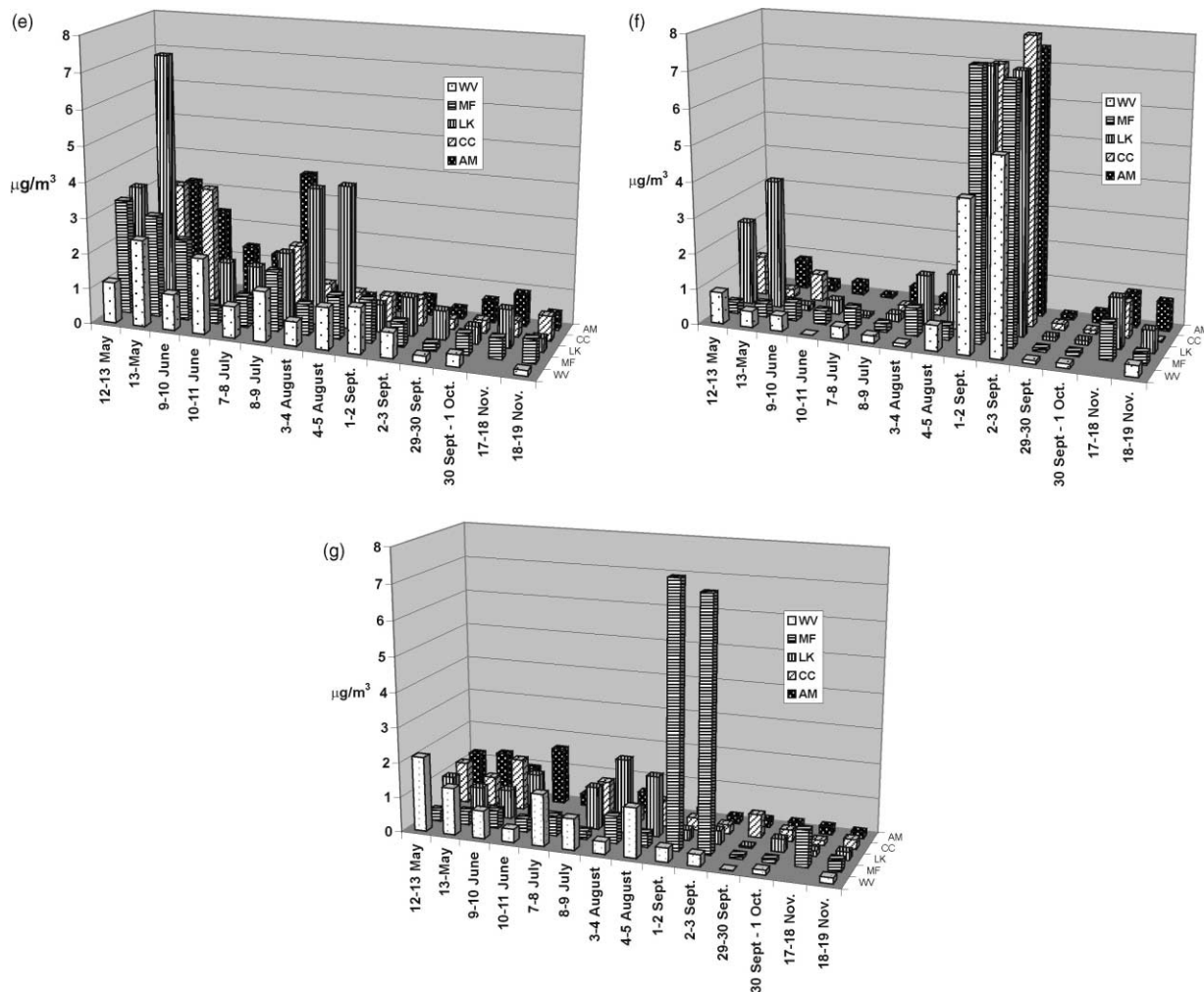


Fig. 6. (Continued).

Concentrations of NO and NO₂ were low with maximum 1-h values below 25 and 35 ppb, respectively. Average 2-week long NO₂ concentrations determined with passive samplers were below 3 ppb. Concentrations of NO and NO₂ determined in Sequoia National Park are similar to other forest locations in California mountains where maximum hourly average NO levels do not exceed 25 ppb, while the NO₂ concentrations were below 50 ppb (Bytnerowicz and Fenn, 1996). Concentrations of these gases are higher in urban areas. In California, the summer time maximum hourly NO concentrations in 1993 ranged between 5 and 150 ppb and the NO₂ concentrations between 10 and 260 ppb in urban agglomerations (California Air Resources Board, 1993). At the levels found in Sequoia National Park no direct negative effects of NO₂ on vegetation are expected (Bytnerowicz et al., 1998).

Nitric acid concentrations were similar to the values determined in other western Sierra Nevada locations in some earlier studies (Bytnerowicz and Fenn, 1996). These values were also similar to the concentrations

recorded at Barton Flats, a moderately polluted site in the San Bernardino Mountains (Bytnerowicz et al., 1999). The highest 24-h average concentrations of HNO₃ at Tanbark Flat of the San Gabriel Mountains, southern California, reached 15.9 with seasonal mean of 11.7 µg/m³ (Grosjean and Bytnerowicz, 1993). In contrast, at the Eastern Brook Lake, eastern Sierra Nevada, summer mean value for HNO₃ was 0.4 µg/m³ (Miller and Walsh, 1991). Ambient concentrations of HNO₃ at Sequoia National Park locations were below the levels that could cause direct damage to vegetation (Bytnerowicz et al., 1998). However, due to its high deposition velocity, the pollutant may provide substantial amounts of N to forest ecosystems (Hanson and Lindberg, 1991).

Nitric acid concentrations in Sequoia National Park were similar to those determined at Whitaker Forest and Shirley Meadow of the western Sierra Nevada (Bytnerowicz and Miller, 1991; Bytnerowicz and Riechers, 1995) and in the San Bernardino Mountains of southern California (Bytnerowicz et al., 1999). Concentrations at

Table 2

Summary of passive sampler results presented as seasonal means with standard deviation (in parentheses), and ranges of concentrations^a

Location	O ₃ (ppb)	HNO ₃ (μg/m ³)	NO ₂ (ppb)
Ash Mountain (AM)	64 (8) ab 53–75	2.9 (0.9) a 1.6–4.2	1.7 (0.3) ab 1.2–2.2
Three Pole Corner (TPC)	72 (10) a 55–85		
Crystal Cave (CC)	52 (7) cd 42–66	0.8 (0.4) bc 0.5–1.5	1.3 (0.5) b 0.9–2.2
Lower Kaweah (LK)	60 (10) bc 44–77	1.1 (0.5) b 0.4–1.7	2.0 (0.6) a 1.3–2.8
Stony Creek (SC)	48 (7) d 39–60	0.6 (0.2) bc 0.3–1.0	1.1 (0.3) b 0.6–1.6
Marble Fork (MF)	46 (7) d 39–58	0.6 (0.2) bc 0.3–1.0	1.1 (0.1) b 0.9–1.2
Huckleberry Meadow (HM)	58 (8) bc 46–71	0.8 (0.4) bc 0.1–1.2	1.2 (0.5) b 0.6–1.9
Wolverton (WV)	41 (7) d 33–59	0.4 (0.2) c 0.3–1.0	1.0 (0.4) b 0.7–1.7
Little Baldy Saddle (LBS)	63 (9) abc 50–71		
<i>P</i> value	<0.001	<0.001	<0.001

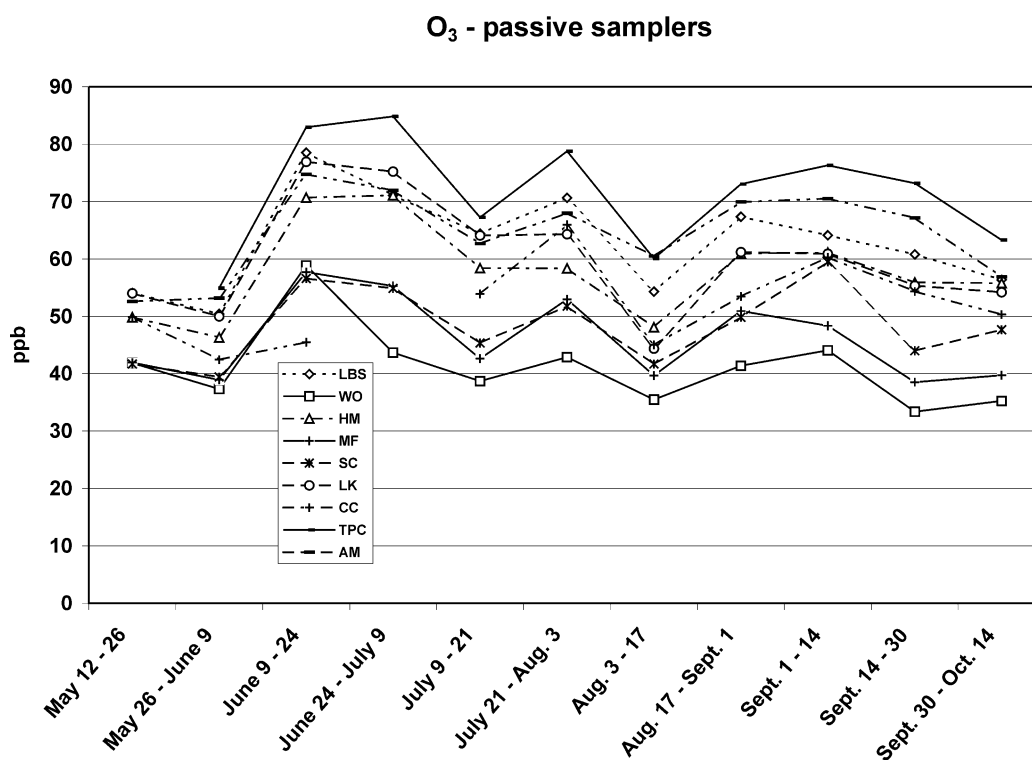
^a Different letters following mean and S.D. indicate significant differences between monitoring sites at a specified “*P*” value.

Fig. 7. Ozone concentrations determined with passive samplers (ppb) expressed as 2-week average values.

Tanbark Flat of the San Gabriel Mountains were higher with seasonal means reaching $0.7 \mu\text{g}/\text{m}^3$ (Grosjean and Bytnerowicz, 1993). In contrast, at Little Valley, eastern Sierra Nevada, HNO₂ concentrations were much lower ($0.003 \mu\text{g}/\text{m}^3$, 24-h average) than the concentrations determined in this study (Bytnerowicz and Fenn, 1996).

No phytotoxic effects of HNO₂ at these levels have been described.

Ammonia concentrations at the higher elevation sites were similar to those found at Whitaker Forest and Shirley Meadow in the western Sierra Nevada (Bytnerowicz and Miller, 1991; Bytnerowicz and Riechers,

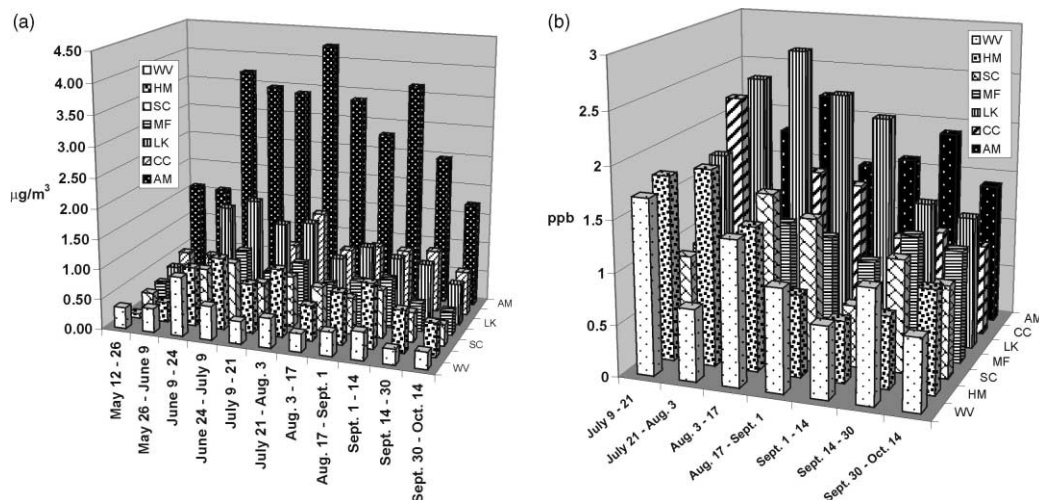


Fig. 8. Concentrations of nitrogenous air pollutants determined with passive samplers expressed as 2-week period average values: (a) HNO₃ and (b) NO₂.

1996). Concentrations of NH₃ at Ash Mountain were significantly higher reflecting proximity of this site to farmlands of the San Joaquin Valley emitting high amounts of the pollutant. Seasonal mean NH₃ concentrations for the mid elevation forests in Sequoia National Park were higher than those determined in the San Bernardino and San Gabriel Mountains of southern California (Grosjean and Bytnerowicz, 1993; Bytnerowicz and Fenn, 1996). At Little Valley, eastern Sierra Nevada, the 24-h average NH₃ concentration was 1.1 µg/m³ (Bytnerowicz and Fenn, 1996). At the remote site of the Canadian Rocky Mountains annual mean NH₃ concentration was 0.3 µg/m³ (Legge and Krupa, 1989). At the levels of NH₃ determined in this study no toxic effects on vegetation are expected (Bytnerowicz et al., 1998). However, due to high deposition velocity of this gas (Hanson and Lindberg, 1991), even moderately elevated concentrations could substantially contribute N to forests may on the western slopes of the Sierra Nevada.

Concentrations of particulate NO₃[−] were within a range of values determined in other western Sierra Nevada locations (Temple and Bytnerowicz, 1993; Bytnerowicz and Riechers, 1995). However, concentrations of particulate NH₄⁺ in Sequoia National Park locations were higher than in other Sierra Nevada locations (Bytnerowicz et al., 2000). Seasonal means were increased by an unexplained surge of NH₄⁺ concentrations in all sampling locations in the beginning of September (Fig. 6f). Similarly high levels of particulate SO₄^{2−} were also found in early September at the Marble Fork site, but stayed low at the remaining sites. In general, the particulate SO₄^{2−} concentrations were low and similar to the values determined in the San Bernardino Mountains (Bytnerowicz et al., 1999) or the Canadian Rocky Mountains (Legge and Krupa, 1989).

In summary, concentrations of nitrogenous air pollutants determined in Sequoia National Park were below phytotoxic levels (Bytnerowicz et al., 1998). From the point of view of nutrient inputs, the N inputs based on stream outflow data in the mid-elevation forests of the Sierra Nevada are negligible (Williams et al., 1995; Williams and Melack, 1997). However, summer time deposition of N pollutants in the most exposed areas of the Sequoia National Park may change nutritional status of some communities. The highest probability of such changes occurs on mesic meadows and riparian areas where summer physiological activity of plants and N uptake directly from air and indirectly from soil may be high.

Sulfur dioxide concentrations were low and typical for California (Böhm, 1992). In the 1993 summer season at Barton Flats of the San Bernardino Mountains, SO₂ concentrations were in a range of 0.3–1.3 µg/m³ (Bytnerowicz et al., 1999). At Tanbark Flat of the San Gabriel Mountains monthly average SO₂ concentrations were higher in summer 1985 and ranged from 0.5 to 3 µg/m³ (Bytnerowicz et al., 1987). Such concentrations do not pose a threat to vegetation (Kozłowski and Constantinedou, 1986). Similarly, concentrations of SO₄^{2−} were low and in the range of concentrations typically found in the western United States. Low levels of S air pollution found in the Sierra Nevada are typical for California and other western states in contrast to high concentrations commonly occurring in eastern parts of the United States (Böhm, 1992).

4.2. Spatial distribution of pollutants

The highest seasonal average O₃ concentration was determined at the Three Pole Corner (71.5 ppb), the well-exposed mid-elevation site in the lower Kaweah/

Marble Fork drainage. At the lowest elevation site, Ash Mountain, O₃ concentrations were lower (64 ppb), although the differences between the two sites were not significant. After reaching peak values at the Three Pole Corner site, O₃ concentrations decreased with increasing elevation and distance from the San Joaquin Valley: Lower Kaweah (60 ppb), Marble Fork (46 ppb), and Wolverton (41 ppb). Crystal Cave, although located at lower elevation, had less O₃ (53 ppb) than Lower Kaweah (Fig. 9). While Lower Kaweah is a well-exposed site on the Kaweah/Marble Fork main drainage, Crystal Cave is located in a small valley branching from the main drainage and lacks direct exposure to the main plum of the polluted air masses. Three other sites outside of the Kaweah/Marble Fork drainage varied from low O₃ levels at Stony Creek (48 ppb), moderate levels at Huckleberry Meadow (58 ppb), and high levels at Little Baldy Saddle (63 ppb). Apparently, concentrations of O₃ in these sites depend on their local patterns of airflow.

In the Sierra Nevada, diminishing O₃ levels with increasing elevation and distance from the pollution source area confirm similar observations made in the San Bernardino Mountains of southern California. After reaching peak values at 1525 m, O₃ concentrations significantly dropped with increasing elevation and distance from the Los Angeles Basin (Bytnerowicz et al., 2000). Our findings do not confirm a phenomenon reported by Brace and Peterson (1998) and Cooper and

Peterson (2002) of O₃ concentrations consistently increasing with elevation in the Mount Rainier National Park and Puget Sound region, Washington. On the Kaweah/Marble Fork transect, dilution of the polluted air masses with distance and O₃ deposition to vegetation exceeded a potential for additional O₃ formation from its precursors.

Nitrogen dioxide concentrations at Ash Mountain and Lower Kaweah were similar and significantly higher than the concentrations recorded at other locations (Table 2). No relationship between concentrations of the pollutant and elevation change was found. Concentrations of HNO₃ significantly diminished as elevation increased along the Kaweah/Marble Fork drainage (Fig. 10). This reflects high affinity of HNO₃ to landscape features due to its high deposition velocity to various surfaces and substantial stomatal uptake by vegetation (Hanson and Lindberg, 1991). Similarly to HNO₃, concentrations of NH₃ significantly decreased with increasing elevation (Fig. 10). Ammonia deposition velocity to vegetation may be even higher than of HNO₃, mainly due to very high stomatal uptake (Hanson and Lindberg, 1991). Ammonia and HNO₃ readily react producing ammonium nitrate (NH₄NO₃). This reaction could cause a significant depletion of HNO₃ and NH₃ concentrations between the source and receptor areas. A significant increase of particulate NO₃⁻ and NH₄⁺ concentrations between the low elevations Ash Mountain and mid-elevation Lower Kaweah was recorded.

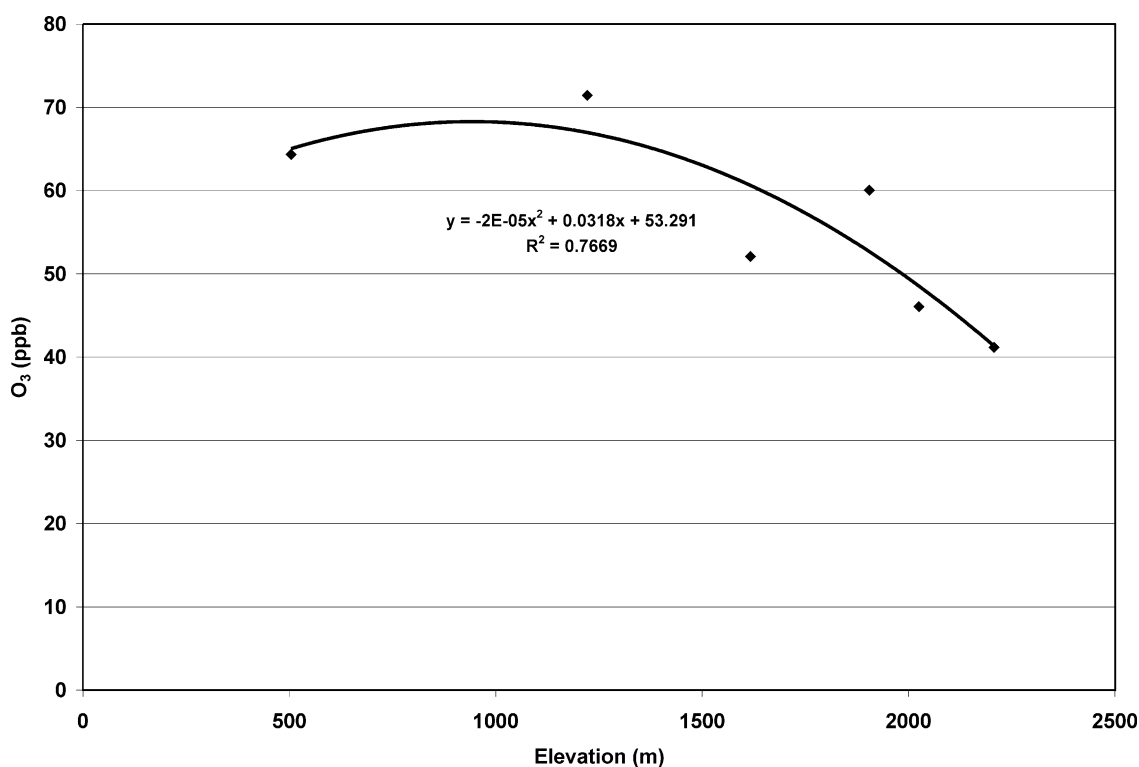


Fig. 9. Changes of seasonal average O₃ concentrations along the Kaweah/Marble Fork drainage: Ash Mountain—504 m; Three Pole Corner—1222 m; Crystal Cave—1617 m; Lower Kaweah—1905 m; Marble Fork—2025 m; and Wolverton—2207 m.

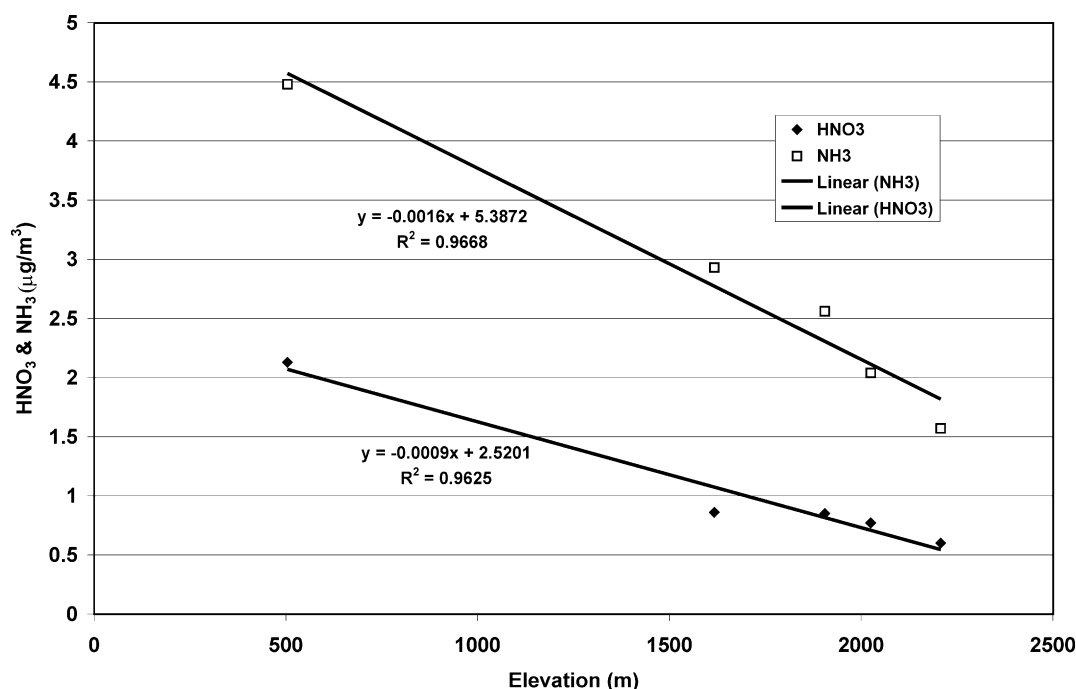


Fig. 10. Changes of seasonal average concentrations of HNO₃ and NH₃ measured with honeycomb denuder/filter pack systems along the Kaweah/Marble Fork drainage: Ash Mountain—504 m; Crystal Cave—1617 m; Lower Kaweah—1905 m; Marble Fork—2025 m; and Wolverton—2207 m.

For both N particulate components, reduction of concentrations between the Lower Kaweah site and the higher elevation sites (Marble Fork and Wolverton) was evident (Table 1). A sum of all N gaseous and particulate compounds measured with the honeycomb denuder systems was higher at the Lower Kaweah site than in the lower elevation Crystal Cave site and was caused by high seasonal means of HNO₂ and particulate NO₃⁻ and NH₄⁺ at that location (Table 1, Fig. 11).

Concentrations of SO₂ at the low elevation Ash Mountain site and the most westerly exposed sites of Crystal Cave and Lower Kaweah were significantly higher than the high elevation, remote sites of Marble Fork and Wolverton (Table 1, Fig. 6d). No clear trends in spatial distribution of SO₄²⁻ were observed (Table 1, Fig. 6g).

4.3. Seasonal and diurnal distribution of the pollutants

Diurnal changes of O₃ concentrations at the Sequoia National Park locations were similar to those reported for Mountain Home, Shaver Lake and Sly Park, the high elevation sites in the western Sierra Nevada (Van Ooy and Carroll, 1995). Lowest concentrations of about 40 ppb occurred at 07:00 PST and reflected decomposition of O₃ from a previous day accelerated by titration by NO from the early morning automobile emissions (Turco, 1997). Ozone concentrations gradually increased with rising temperature and solar radiation, reaching peak values in the late afternoon (17:00 PST).

Contrary to what could have been expected, the peak O₃ values occurred at the same time at the low elevation site (Ash Mountain) and the two higher elevation locations (Lower Kaweah and Wolverton). Pronounced diurnal changes of O₃ concentrations in the monitored sites indicate their strong dependence on photochemical smog formed in the San Francisco Bay and San Joaquin Valley pollution source areas. Diurnal distribution of ozone concentrations in the San Bernardino and San Gabriel Mountains of southern California were similar and strongly affected by the Los Angeles urban plume (Miller et al., 1986; Bytnerowicz et al., 1987).

No clear differences in distribution of NO concentrations during the season occurred. However, highest levels of NO₂ were recorded in the first half of August. Low values in the second half of September may reflect diminished oxidation of NO at lower light intensities and temperatures. Increasing concentration of NO₂ starting in the middle of October could result from wood burning in the Park as well as in Three Rivers and other nearby low-elevation communities.

In the beginning of August prescribed forest fires were taking place in the vicinity of Lower Kaweah and probably led to elevated HNO₂ concentrations at Lower Kaweah (Fig. 6c). This phenomenon is caused by rapid reduction of NO₂ released during fires to HNO₂ on suspended soot aerosol particles (Kalberer et al., 1999). Concentrations of particulate NO₃⁻ and NH₄⁺ were also elevated at the Lower Kaweah site during that period (Fig. 6e, f). The highest levels of NO₂ occurred at Lower Kaweah, where probably the most effective oxidation of

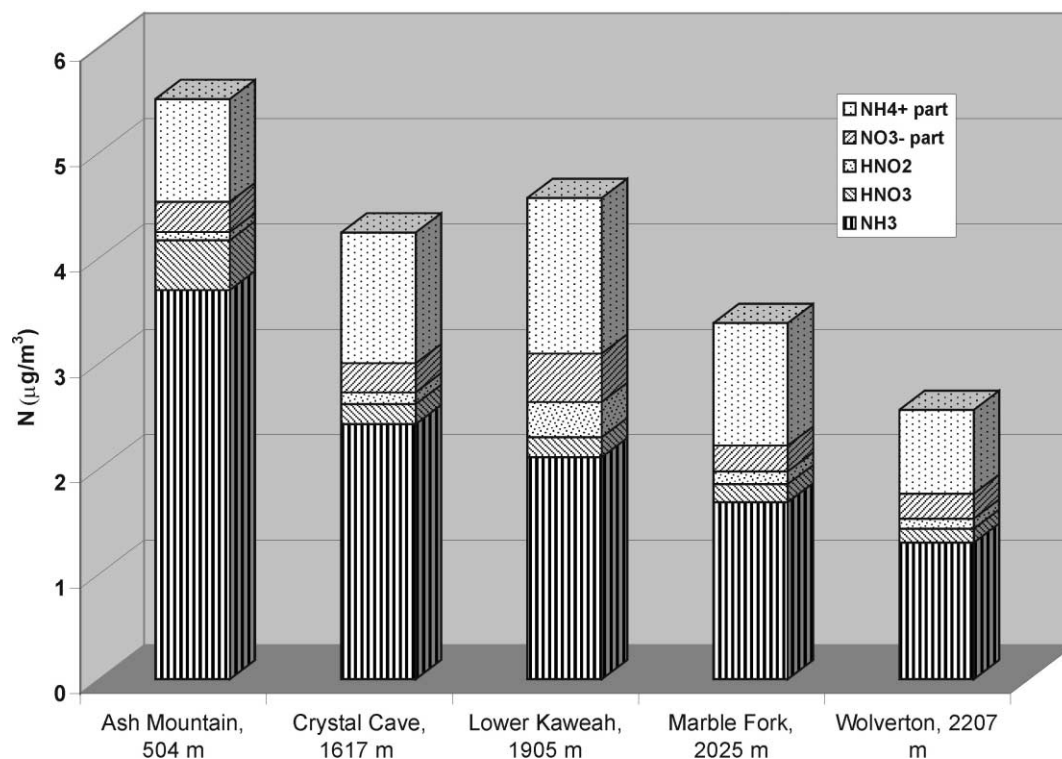


Fig. 11. Changes in concentrations of nitrogenous pollutants measured with honeycomb denuder/filter pack systems along the Kaweah/Marble Fork drainage.

NO by O₃ on the Kaweah/Marble Fork drainage took place.

4.4. Apportionment of N pollutants

A budget of nitrogenous compounds was calculated based on results from an active NO/NO_x analyzer and honeycomb denuder/filter pack systems at the Lower Kaweah site during the 7 July–1 October 1999 period. Oxidized N compounds were less abundant than the reduced components resulting mainly from agricultural activities in the San Joaquin Valley. Ammonia comprised 34% of all inorganic N species measured, followed by NO₂ (30%), particulate NH₄⁺ (22%), particulate NO₃⁻ (5%), HNO₂ (4%), HNO₃ (3%), and nitric oxide (2%) (Fig. 12). Similarly higher proportion of N reduced compounds (about 57%) was determined in 1988–1990 at the nearby Whitaker Forest (Bytnerowicz and Riechers, 1995). Compared with Whitaker Forest, the Lower Kaweah site had higher proportion of particulate NH₄⁺ (22% versus 10%), probably because of its higher elevation (1905 m versus 1600 m) and more time for formation of secondary particulate pollutants. At Tanbark Flat in the San Gabriel Mountains (within the Los Angeles air basin), most of N air pollutants were in an oxidized form, indicating a strong influence of urban automobile emissions (Bytnerowicz and Fenn, 1996). Our data suggest that in summer the urban-polluted air masses transported from the San Francisco

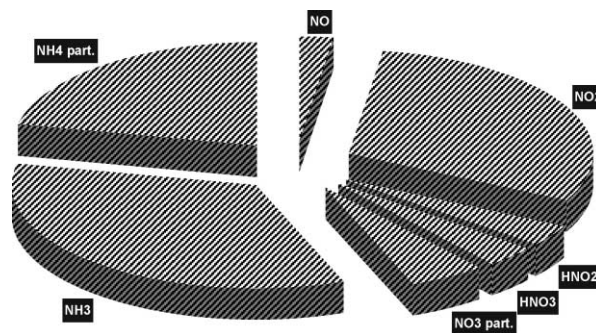


Fig. 12. Apportionment of N gaseous and particulate pollutants at the Lower Kaweah site.

Bay Area and the San Joaquin Valley (California Surface Wind Climatology, 1984) provide less N into Sequoia National Park than agricultural activities in the San Joaquin Valley.

5. Conclusions

Results of this study indicate that concentrations of O₃, HNO₃, and NH₃ in Sequoia National Park were elevated. However, while phytotoxic effects due to O₃ exposures for sensitive species may be expected, neither HNO₃ nor NH₃ are high enough to result in injury to vegetation. From a biogeochemical perspective, even slightly elevated concentrations of N pollutants may

provide substantial amount of N to forest environment. In the western United States characterized by low levels of available N, both wet and dry deposition of N, can affect growth of trees and other species. However, these levels are insufficient to be detected in stream outflows.

Our study indicated clear patterns of air pollution distribution along a major drainage of Sequoia National Park, the Kaweah/Marble Fork Valley. Significant decline of O_3 , HNO_3 , NH_3 and SO_2 concentrations was shown with increasing elevation and distance from the pollution source area. For particulate NO_3^- and NH_4^+ the highest concentrations were recorded in the mid-elevation site. This phenomenon can be explained by generation of NH_4NO_3 from reactions of gaseous HNO_3 and NH_3 during their transport along the drainage. Similarly to other western Sierra Nevada locations, majority of N inorganic species is in a reduced form as NH_3 and NH . This indicates an importance of agricultural emissions on nutritional budget of the western Sierra Nevada forests and other ecosystems.

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