

Vertical Distribution of Ozone and Nitric Acid Vapor on the Mammoth Mountain, Eastern Sierra Nevada, California

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In August and September 1999 and 2000, concentrations of ozone (O₃) and nitric acid vapor (HNO₃) were monitored at an elevation gradient (2184–3325 m) on the Mammoth Mountain, eastern Sierra Nevada, California. Passive samplers were used for monitoring exposure to tropospheric O₃ and HNO₃ vapor. The 2-week average O₃ concentrations ranged between 45 and 72 ppb, while HNO₃ concentrations ranged between 0.06 and 0.52 µg/m³. Similar ranges of O₃ and HNO₃ were determined for 2 years of the study. No clear effects of elevation on concentrations of the two pollutants were detected. Concentrations of HNO₃ were low and at the background levels expected for the eastern Sierra Nevada, while the measured concentrations of O₃ were elevated. High concentrations of ozone in the study area were confirmed with an active UV absorption O₃ monitor placed at the Mammoth Mountain Peak (September 5–14, 2000, average 24-h concentration of 56 ppb).

KEY WORDS: ozone, nitric acid vapor, elevation change, passive sampling, active monitoring

DOMAINS: plant sciences, global systems; environmental management and policy, ecosystems management, environmental monitoring

INTRODUCTION

Ambient tropospheric ozone (O₃) results from production in the free troposphere, injection from the stratosphere to the troposphere, photochemical production, photolysis, dry deposition, and chemical destruction[1]. Stomatal uptake of vegetation, especially by forest canopies, may significantly affect ambient O₃ concentrations[2]. First measurements of tropospheric O₃ concentrations made between 1876 and 1910 at Montsouris near Paris showed background levels of ~10 ppb[3]. Concentrations of O₃ increase gradually in the Northern Hemisphere — over the last 30 years, 1–2% annual increase of O₃ concentrations has been recorded in Europe[4]. At present, O₃ concentrations of >50–60 ppb are often measured as the background levels[5]. O₃ is a criteria pollutant affecting human health at elevated concentrations[6]. It has been well

established that O₃ may be toxic to vegetation at concentrations >30–40 ppb and that severity of plant damage depends on a length and characteristics of the exposure and various abiotic and biotic factors[7,8,9].

In dense urban areas such as southern California, nitrogen oxides are a major component of photochemical smog. During the photochemical smog formation process, nitric oxide (NO) is rapidly oxidized to nitrogen dioxide (NO₂) that subsequently reacts with hydroxyl radicals producing nitric acid (HNO₃) vapor[10,11]. While NO₂ is often the dominant nitrogenous (N) pollutant[12,13], HNO₃ vapor may be more relevant to problems associated with N deposition to forests and other ecosystems because of its unusually high deposition velocity[14,15]. In areas of high ambient concentrations, HNO₃ may also exhibit direct toxic effects on foliage of forest vegetation[16].

Concentrations of O₃ and HNO₃ vapor in areas affected by photochemical smog are strongly correlated in several locations in the Los Angeles Basin[17]. However, in mountain locations down-wind from the photochemical source areas, concentrations of HNO₃ decrease more rapidly than those of O₃ due to high deposition velocity of HNO₃ vapor[18].

There is a rapidly growing interest in passive sampling systems for quantifying exposure to ambient concentrations of gaseous air pollutants. Excluding the laboratory analysis costs, passive samplers are inexpensive, easy to use, and do not require electricity to operate. Therefore, they are very attractive for use in remote and wilderness areas and for regional scale air-quality assessments[19]. Application of passive samplers has allowed acquisition of important information on spatial and temporal distribution of O₃ exposure for the entire Sierra Nevada range[20,21] and O₃, NH₃, NO₂, and HNO₃ in Sequoia National Park[22].

Sierra Nevada Mountains are the primary topographic feature of the state of California. These mountains have tremendous ecological, economical, and recreational values[23]. Sierra Nevada is quite diversified in regard to air pollution distribution. Western slopes of the Sierra Nevada are strongly affected by pollution generated in the San Francisco Bay and Central Valley[24], while the eastern Sierra Nevada has been regarded as a clean area with relatively low pollutant concentrations[25,26,27]. The Mammoth Mountain near Mammoth Lakes in Eastern Sierra Nevada (Fig. 1) is a popular recreational location for millions of Californians, as well as visitors from other states and abroad.

METHODOLOGY

Air pollution monitoring on the Mammoth Mountain was performed during the summer class "Acquisition and Analysis of Environmental Data," organized by the Department of Environmental Sciences of the University of California in Riverside. The O₃ passive samplers[28] produced by Ogawa & Co., USA, Inc., and HNO₃ samplers[30] were used. The samplers were exposed from August 20 to September 7, 1999, and from August 21 to September 6, 2000, at locations presented in Fig. 2 and described in Table 1. Passive samplers were placed about 2 m above the ground on PVC poles — each sampler contained two replicate filters subsequently used for analyses. Nitrate from the O₃ samplers' filters, a product of nitrite oxidation by O₃, was extracted with nanopure water and determined with ion chromatography (Dionex 4000i)[28,29]. Nitrate from nylon filters, a product of HNO₃ absorption, was also extracted with nanopure water, and its concentrations were determined colorimetrically (TRAACS 2000 Bran & Lueble Instrument)[30,31]. O₃ passive samplers were calibrated against a UV-absorption instrument (Thermo Environmental Model 49) located nearby in Yosemite National Park. HNO₃ samplers were calibrated against honeycomb denuder systems in continuously stirred tank reactor (CSTR) chambers located at the University of California in Riverside[32]. Between September 5 and 14, 2000, concentration of O₃ at the Mammoth Mountain Peak were also measured with a 2B Technologies UV-absorption instrument[33].

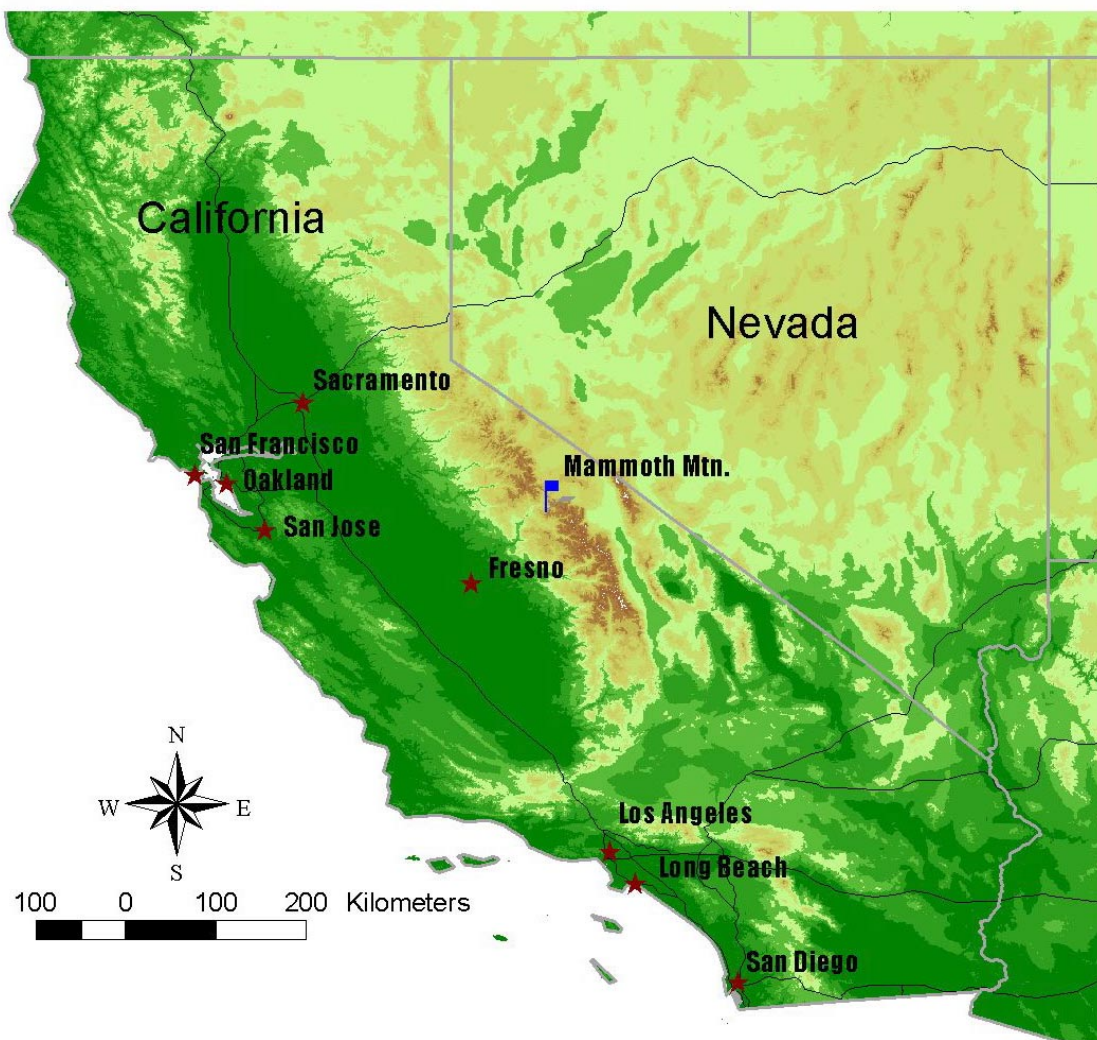


FIGURE 1. Location of Mammoth Mountain in Sierra Nevada, California.

TABLE 1
Location and Elevation of Monitoring Sites on Mammoth Mountain

Site Number	Name	Elevation (m)	
		1999	2000
1	Rainbow Falls	2267	2184
2	Starkweather Lake	2416	2416
3	Agnew Meadows	2591	2688
4	Minaret Summit	2810	2810
5	Chair 14	3152	3152
5B	Deadman's Pass	-	3135
6	Mammoth Mountain Summit	3350	3325

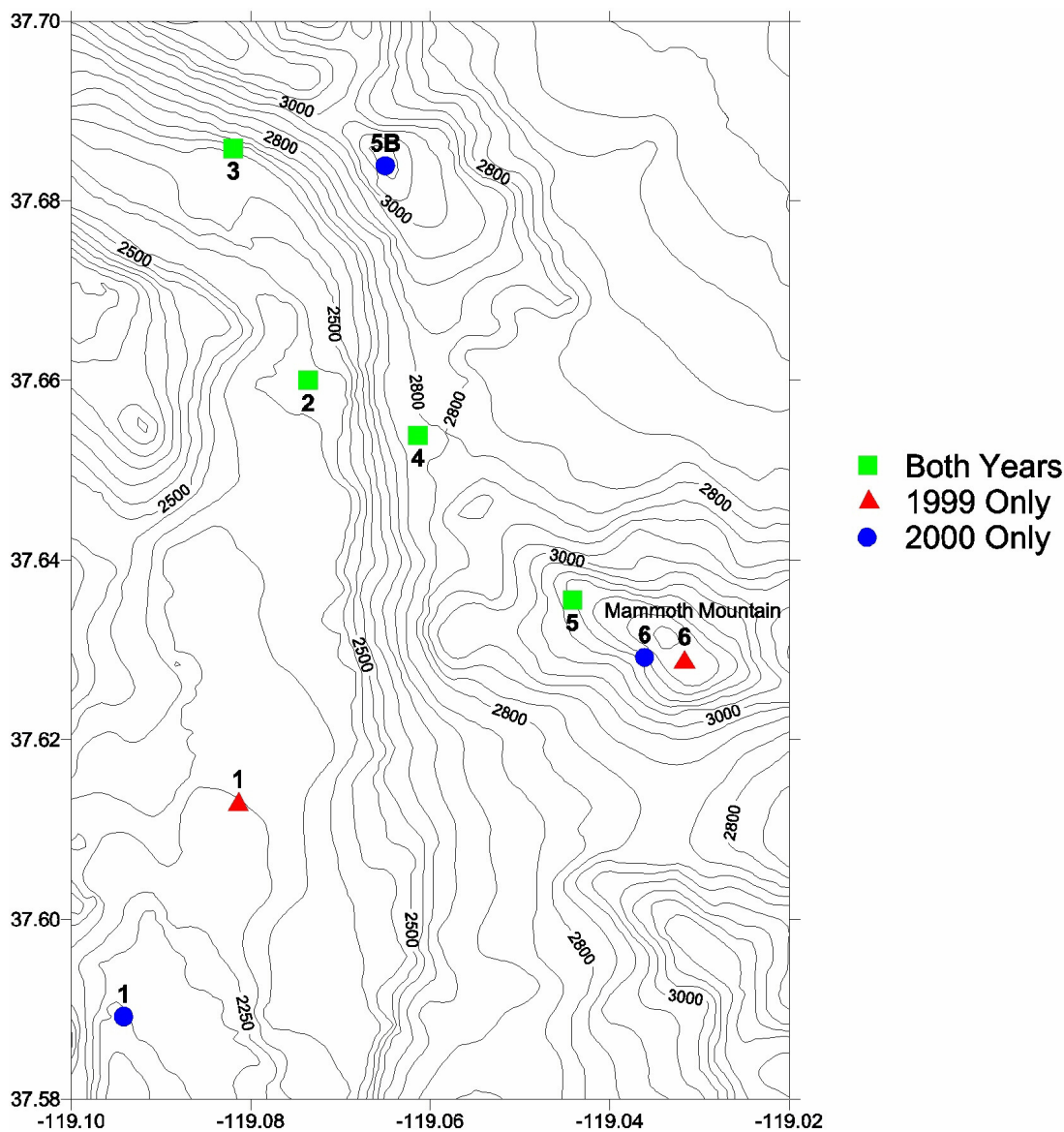


FIGURE 2. Location of monitoring sites on Mammoth Mountain.

RESULTS AND DISCUSSION

Ozone

Concentrations of O₃ in 1999 increased with elevation up to 2810 m (Minaret Summit site), decreased at 3152 m (Chair 14), and increased to the highest level of 72 ppb at 3330 m (Mammoth Mountain Peak). In 2000 no clear effect of elevation on O₃ concentrations was recorded. O₃ concentrations at the 2416-, 2688-, 2810-, and 3152-m sites (Starkweather Lake, Agnew Meadows, Minaret Summit and Chair 14, respectively) were similar to the 1999 values. However, when in 2000 the Rainbow Falls site was moved to the more exposed but lower elevation location, the O₃ concentrations significantly increased. On the other hand, when location of the passive sampler on the Mammoth Mountain Peak was moved 25 m lower, the O₃ concentrations decreased (Fig. 3).

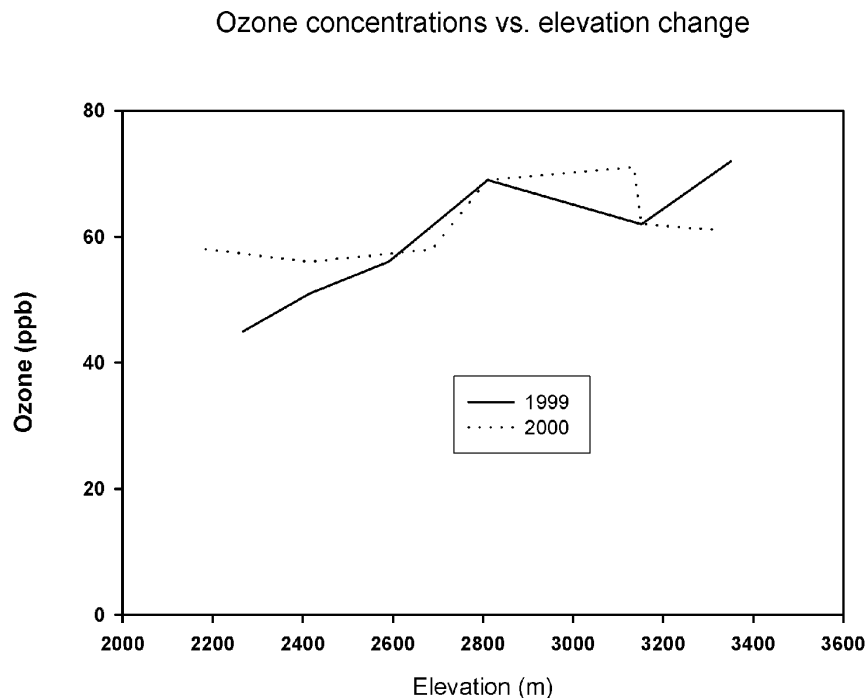


FIGURE 3. Concentrations of O₃ determined with passive samplers on Mammoth Mountain.

Measurements of O₃ concentrations with an active monitor at the Mammoth Mountain Peak confirmed high levels of the pollutant determined with passive samplers near that site during 1999 and 2000 measurements. Diurnal distribution of O₃ concentrations varied between individual days without any particular pattern. Examples of diurnal distribution for 4 days are presented on Fig. 4. The lowest recorded value was 35 ppb on September 12, while during other days O₃ levels stayed >40 ppb. On September 8 the O₃ levels reached 73 ppb. O₃ average concentration for the entire period of active monitoring was 56 ppb (S.D. 10 ppb). These values are similar to those recorded in August 1987 at the nearby Eastern Brook Lake in the eastern Sierra Nevada[34]. These concentrations can be considered as elevated above normal background concentrations for the Sierra Nevada — in other parts of the Sierra Nevada range, far from the photochemical smog source areas, 2-week average O₃ concentrations stayed ~40 ppb[35,36]. Persistence of high O₃ levels and a lack of clear diurnal patterns indicated that the pollutant originated in a remote pollution source area, either in California Central Valley or southern California. Transport of polluted air masses from southern California through the Tehachapi and Cajon Passes takes place[37], therefore increased levels of the pollutant along the eastern Sierra Nevada should be considered. If these were true, the expected concentrations of O₃ at sites located more to the south and closer to the source area would be higher. However, results of recent air-quality measurements indicate that concentrations of O₃ in the Bishop area (maximum 8-h average concentrations ~60 ppb) are much lower than at Mammoth Lakes located about 70 km to the north (maximum 8-h average concentrations ~100 ppb)[38]. Therefore, a possibility of transport of the polluted air masses from California Central Valley across the Sierra Nevada seems to be more plausible. We suggest that polluted air masses from the Fresno area in the San Joaquin Valley (maximum 8-h O₃ average concentrations approaching 126 ppb) may be transported with prevailing summer winds[39] along the San Joaquin River drainage into the Mammoth Mountain area).

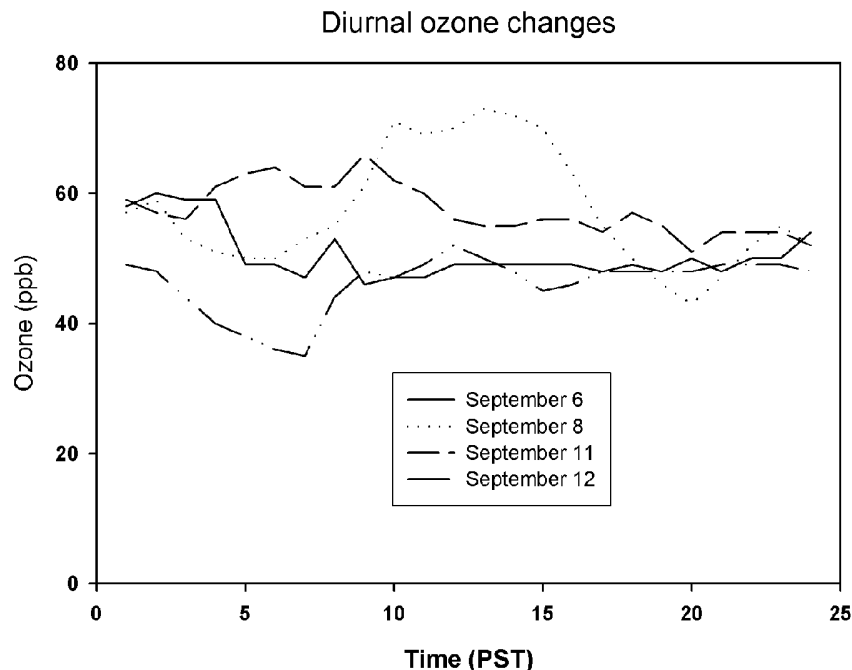


FIGURE 4. Concentrations of O₃ determined with an active UV absorption monitor at the Mammoth Mountain Peak.

Nitric Acid Vapor

During the 1999 study HNO₃ concentrations increased with elevation with an exception of Agnew Meadows (2591 m) that was as low as the lowest-elevation Rainbow Falls site (2267 m). In 1999 the HNO₃ concentrations ranged between 0.06 and 0.52 μg/m³. During the 2000 study no clear relationship with elevation was detected, but ranges of concentrations remained within those seen in 1999 (0.25–0.42 μg/m³). In general, the detected HNO₃ concentrations were at low background levels and similar to 0.36 μg/m³ summer average detected in the nearby Eastern Brook Lakes[27]. These results are also similar to other remote mountain locations in North America[40]. In the western Sierra Nevada HNO₃ levels are higher — at Whitaker Forest the 24-h average daytime HNO₃ concentration in summer of 1990 was ~1.1 μg m⁻³[41]. At high elevation locations in Sequoia National Park, 2-week long average HNO₃ concentrations ranged between 0.04 and 1.4 μg/m³ in summer 1999[42]. In the moderately polluted Barton Flat site of the San Bernardino Mountains, the average 24-h concentrations HNO₃ ranged from 3.0 to 6.5 μg m⁻³ during the 1993–1995 summer seasons[16]. Although we assume that polluted air from the San Joaquin Valley contained high concentrations of O₃, concentrations of HNO₃ were drastically depleted compared to the source area due to a very high reactivity of the pollutant[14] and deposition to rocks and vegetation before reaching the receptor area. At the HNO₃ levels recorded at the Mammoth Mountain, no phytotoxic effects or significant levels of nitrogen deposition to natural ecosystems can be expected[43].

This study indicated that application of relatively simple techniques such as passive sampling offers new opportunities for evaluation of air quality in remote locations. Such information is urgently needed, especially for land managers of ecologically important areas. The Mammoth Mountain is in close vicinity of the John Muir and Ansel Adams Wilderness areas. These important Class I areas require special federal protection and should have good air quality for protection of sensitive flora and fauna and for well-being of numerous local inhabitants and visitors coming for recreation and rest.

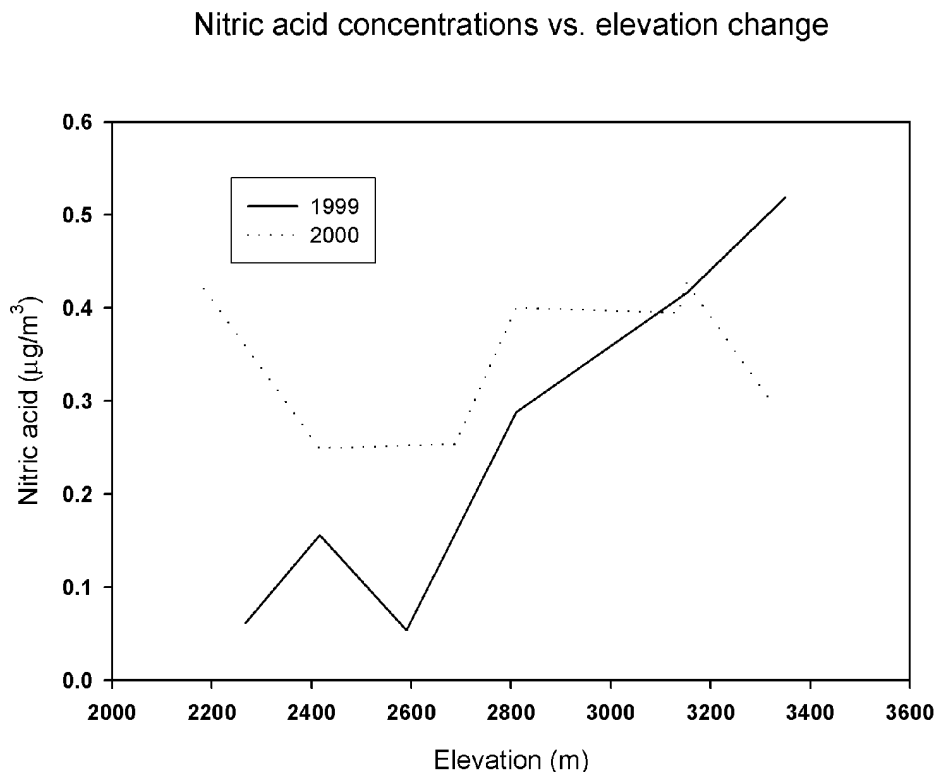


FIGURE 5. Concentrations of HNO₃ determined with passive samplers on the Mammoth Mountain.

CONCLUSION

The Mammoth Mountain in the eastern Sierra Nevada is exposed to O₃ concentrations that are elevated above background. This was not expected in this location, which is distant and separated from the photochemical smog source areas by the Sierra Nevada range. A possibility of a trans-Sierra Nevada transport of polluted air masses from the polluted San Joaquin Valley is high.

HNO₃ vapor concentrations, however, were low and at the expected background levels may not pose a threat to natural resources or to humans of the investigated area.

This study showed that passive samplers are very useful for monitoring of air pollutants in remote mountain locations. Such samplers can also serve as simple educational tools for students interested in environmental pollution problems.

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