Abstract:

During the summer of 2012, air quality data had been collected from different sites around the Lake Tahoe Basin; these sites included Homewood, Heavenly (south lake), and the Tahoe Regional Planning Agency headquarters (near the state line). The data had been used to augment ozone data collected in 2010. Examination of both data sets allowed for the interpretation of the ozone, nitrogen oxides, and volatile organic compound status of Lake Tahoe. It had been observed that: Lake Tahoe experiences a common midday ozone concentration of approximately 55 parts per billion (volume). Having analyzed the data, quite apparent is the fact that much of the ozone in Lake Tahoe can be attributed to air parcels traveling in to the basin from the Sacramento Valley. The nitrogen oxide concentrations were observed to be relatively low around the basin, however, one site (TRPA) observed high enough concentrations to be considered NO$_x$ (nitrogen oxide) saturated.
Introduction

Ambient concentrations of primary and secondary pollutants in and around the Lake Tahoe Basin are of prominent importance to environmental groups, government agencies such as the EPA, and anyone with an interest in preserving the air and water quality at Lake Tahoe. The Lake Tahoe area, until recently, might have been construed to be a relatively clean location with regards to air quality. At this point in time however, O₃ concentrations in the basin are a major concern because they occasionally approach the recently revised EPA standard for 8-hour average concentrations of 75 parts per billion.

Background info on Ozone

Ozone is the triatomic allotrope of oxygen. It is a secondary pollutant that is typically formed from the photolysis of NO₂. Photolysis can only occur during the daylight hours, therefore, ozone will only be created during the day. During the evening hours, ozone concentrations can decrease due to a number of factors including dry plant deposition, and nitric oxide titration. It is important to note that NO₂ is also, for the most part, a secondary pollutant and is produced and replenished by a free radical chain reaction involving the hydroxyl radical and reactive volatile organic compounds or VOCs (see appendix A). This chain reaction leads to an important relationship between the concentration of VOCs and that of oxides of nitrogen (NOₓ: defined as NO + NO₂) in determining ambient air quality. The most general form of an equation representing the production of ozone is given below.

\[ \text{VOC} + \text{NO}_x + \text{Sunlight} \rightarrow \text{O}_3 \quad \text{Eq.1} \]

Ozone has been designated a criteria pollutant by the EPA and is in fact the principle ingredient in urban smog. Ozone is harmful to humans, wildlife and vegetation because of its
oxidizing capability. Pre-Industrial background ozone concentrations are estimated to have been in the range of 10-20 parts per billion (by volume). Today, remote areas usually have background ozone concentrations of approximately 20-40 ppbv. Lake Tahoe is well past this benchmark and it appears to be on its way into moderate-to-high ozone territory.

**Experimental Methods**

Multiple devices had been used to measure the ambient concentrations of ozone around the basin. Included in this array were multiple 2B Technologies external pump ozone monitors. Calibration of these devices was not necessary as the Beer-Lambert spectral calculation is performed using a relative zero (see appendix D). For the oxides of nitrogen measurements, two 2B technologies monitors, each with a similar theory of operation to that of the ozone monitors, had been placed at the lower Homewood site; while two other nitric oxide monitors with greater precision and accuracy (standard deviation of approximately 0.5 ppb) had been placed at the Heavenly site and at the Upper Homewood site. At each of the four sites, the instruments were set to take measurements and record five minute (ozone monitors) and one minute averages (oxides of nitrogen monitors).
Results

Data Group 1: Ozone and Oxides of Nitrogen Concentration Hourly Values for Entire Week

Figure 1: Ozone All Sites

Above: plot representing average hourly values of ozone concentrations (ppbv) at all 2012 sites.
Above: plot representing average hourly values of oxides of nitrogen concentrations (ppbv) at all 2012 sites.
Figure 3: Lower Homewood Full Week Summary

Above: plot summarizing ozone and oxides of nitrogen concentrations for the Lower Homewood site (2012).
Figure 4: Upper Homewood Full Week Summary

Above: plot summarizing ozone and oxides of nitrogen concentrations for the Upper Homewood site (2012).
Figure 5: Heavenly Site Full Week Summary

Above: plot summarizing ozone and oxides of nitrogen concentrations for the Heavenly site (2012).
Figure 6: TRPA Full Week Summary

Above: plot summarizing ozone and oxides of nitrogen concentrations for the TRPA site (2012).
Data Group 2: Diurnal Trend Plots for Ozone and Oxides of Nitrogen

Figure 7: Ozone All Sites

Above: diurnal plot representing average ozone concentrations for specified hour of day.
Figure 8: NOx All Sites

Above: diurnal plot representing average oxides of nitrogen concentrations for each specified hour of the day.
Above: diurnal plot representing average ozone to oxides of nitrogen ratio for each specified hour of the day.
Figure 10: TRPA O₃, NO,NO₂, O₃:NOₓ Ratio

Above: diurnal plot summarizing all relevant parameters measured at the TRPA site (2012).
Figure 11: TRPA Diurnal Data Summary

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Above: table of ratios and diurnal average concentrations represented in the plots on the previous pages.
Discussion

Figure 1 (displaying hourly ozone data for the entire week) shows recurring diurnal trends in ozone concentrations. A slight dip in ozone concentration can be observed around Julian day 205. This is most likely due to a steady rainstorm\(^1\) that began on that day. Ozone is very soluble in water, such that precipitation events usually correlate with a drop in observed ozone concentrations\(^2\).

Ozone Trends Observed during the Daylight Hours

Data collected during the 2012 study, like those collected in 2010 (see appendix B) displayed elevated ozone concentrations at all sites during the well-mixed middle of the day period (see appendix C for comparisons with different sites in California). Note that a common concentration of approximately 53-55 parts per billion (volume) can be observed around the basin (see Figure 7 for diurnal plot).

It is not plausible that each of these sites would witness exactly the same amount of local photochemical production of O\(_3\) as to allow for such consistency (the values are within one standard deviation of one another). Also worth noting as evidence is that the values for nitrogen oxides are quite low at most sites (see Figures 3 through 6) thus it would not be expected that the increase in ozone concentrations observed in the middle of the day is the result of local production as this would require a much larger concentration of NO\(_2\) for photolysis. A more

\(^{1}\) Precipitation data California Data Exchange Center, Department of Water Resources. http://cdec.water.ca.gov/cgi-progs/staMeta?station_id=WC3
likely hypothesis is that the Lake Tahoe basin is the (well-mixed) destination of air parcels containing ozone and ozone precursors, so that what is measured is actually “background” (ozone) that has been transported into the Basin.

**Ozone Trends Observed during the Nocturnal Hours**

While there is an approximately “common” ozone concentration observable from late morning to the afternoon, discrepancies do exist between the different sites at night and in the early morning. Most conspicuously, Upper Homewood does not appear to adhere to an expected diurnal trend (high [O$_3$] during the day, low [O$_3$] at night). This observation is easily explained. Upper Homewood, being that it is at a relatively high altitude (7872 ft), maintains its exposure to the free troposphere and is therefore replenished with ozone rich air during the night (via regional transport of ozone rich air from the west) while the rest of the sites, covered by the temperature inversion$^3$, are not exposed to additional ozone in the evening hours.

**Outside Sources of Ozone and Ozone precursors**

Of great importance is the source of ozone (and ozone precursor) rich air that leads to the background concentrations around the basin. A large number of back trajectories give evidence that this source is most likely the Sacramento Valley (see Figure 12 below). Air is shown to be travelling in from the Pacific Ocean, through the Sacramento valley, up the Sierra

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$^3$ A temperature inversion is an anomaly in the usual relationship between altitude and temperature. Air parcels to not travel effectively through temperature inversions, thus temperature inversions can behave as a cap, closing of exposure to air parcels from higher altitude.
Nevada mountain range and, finally, to the Lake Tahoe Basin. Air quality in the Sacramento valley is therefore of crucial interest to this study and is discussed in detail in appendix C.

**Figure 12: Trajectories of Air Parcels Destined for Lake Tahoe⁴**

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⁴ HYSPLIT Trajectory model, NOAA Resources Laboratory
Above: Plot generated through use of the Hysplit model. Back trajectories were taken for the air parcels that arrived at the Lake Tahoe basin during the week of the study and the preceding week. Trajectories had been recalculated every 12 hours to ensure a greater degree of accuracy.

**Oxides of Nitrogen**

The observed concentrations for the nitrogen oxides are a bit more complex with regard to their daily trends. Both the Heavenly site and the Tahoe Regional Planning Agency site display spikes in NO\textsubscript{x} concentration that are not repeated on a daily basis (see Figure 2). The spikes at the Heavenly site were probably caused by maintenance vehicles and diesel trucks that occasionally drove by the sampling site. TRPA, on the other hand, is located near the Kingsbury Grade highway (see map appendix B) and it is likely that the spikes in NO\textsubscript{x} could be attributed to large amounts of fuel combustion during high traffic hours. Figure 8 reveals that, while overall NO\textsubscript{x} levels are relatively low at Tahoe (See appendix C), there are significant NO\textsubscript{x} concentrations in the area surrounding TRPA. For this reason, TRPA may be serving as a local source of ozone (via photolysis of NO\textsubscript{2}).

**NO\textsubscript{x} and VOC sensitivity at Lake Tahoe**

Before discussing the NO\textsubscript{x} and VOC sensitivities or lack thereof at different sites around the basin, it is first important to define exactly what is meant by the two terms. First, we note that equation 1 is a gross oversimplification of the complete reaction necessary to produce ozone, that in actuality, the volatile organic compound must first initiate a free radical chain reaction by interacting with a hydroxyl radical (see appendix A). Lastly we note that: while both NO\textsubscript{x} and VOCs are required to produce ozone, the VOC is constantly competing with NO\textsubscript{2} for reaction with the hydroxyl radical, and that NO\textsubscript{2} reacts 5.5 times faster with hydroxyl radical than does
the average volatile organic compound\textsuperscript{5}. A simplified (unbalanced) version of the two competing reactions and, in the case of the VOC reaction, those that follow are shown below.

\[
\begin{align*}
\cdot\text{OH} + \text{NO}_2 & \rightarrow \text{HNO}_3, \quad \text{Equation 2} \\
\cdot\text{OH} + \text{VOC} & \rightarrow \text{A} + \text{C} \rightarrow \text{B} + \text{D} \rightarrow \text{O}_3, \quad \text{Equation 3}
\end{align*}
\]

where A,B,C, and D are unspecified intermediates that differ depending on the identity of the volatile organic compound. Because NO\textsubscript{2} reacts 5.5 times faster with hydroxyl radical, the concentration of the volatile organic compounds must be approximately 5.5 times that of NO\textsubscript{2} in order to facilitate the production of ozone. A region is referred to as NO\textsubscript{x} sensitive if the VOC:NO\textsubscript{2} ratio is greater than 5.5:1, and as VOC sensitive if the concentration is below 5.5:1. In the former case, an increase in NO\textsubscript{x} will result in an increase in ozone (as increased NO\textsubscript{2} photolysis can occur without the inhibition of volatile organic compound / hydroxyl radical reactions). In the VOC sensitive case, however, an increase in NO\textsubscript{2} will result in further inhibition of the volatile organic compound / free radical initiation step, as a greater degree of NO\textsubscript{2} /•OH titration will be observed. An optimum rate of production of ozone is attained if the VOC: NO\textsubscript{2} ratio is approximately equal to 5.5:1.

To assess whether a region is VOC or NO\textsubscript{x} sensitive directly, data pertaining to all VOCs would be needed along with accurate data for the NO\textsubscript{2} concentrations. Because it is not entirely feasible to sample all of the volatile organic compounds in a region, certain observation

\textsuperscript{5} Seinfeld, John H., Pandis, Spyros N. *Atmospheric Chemistry and Physics* (pg. 299)
Based methods have been developed\(^6\) to predict the type of sensitivity likely to be observed in a region. These methods examine the ratios of certain parameters, and make inferences pertaining to the type of “sensitivity” of a given region (see appendix E).

The most readily available data that were relevant to these observation based methods were those of NO\(_x\) and O\(_3\) concentrations. By determining the ratio of O\(_3\) to NO\(_x\) (see figure 9), we can estimate the ratio of O\(_3\) to NO\(_y\)\(^7\). Note that this ratio can indeed be used to determine whether a region is NO\(_x\) or VOC sensitive (Appendix E). In determining this ratio one can make some tentative predictions even though NO\(_y\) data are not available.

Figure 9 displays a diurnal plot for the ratio of ozone to oxides of nitrogen (all sites). Comparing these plotted data with the ratios given in Appendix F show that, for the most part, Lake Tahoe is observed to be an NO\(_x\) sensitive regime; that is, most of the sites do not appear to be NO\(_x\) saturated. This is to be expected as Tahoe does not produce an appreciable amount of NO this can be made clear by examining Figures 3 through 5 (above). However, the data collected at the TRPA site indicate that the surrounding area may be in the transition range (from NO\(_x\) sensitivity to NO\(_x\) saturation) if not NO\(_x\) saturated already. This is likely due to the fuel combustion observed at the nearby Kingsbury Grade highway as previously mentioned. Observe Figure 11 and compare the values of the ratios given by the data for O\(_3\) and NO\(_x\) to those listed in appendix E.


\(^7\) NO\(_y\)=NO\(_x\) + all other reactive nitrogen (eg. NH\(_3\), nitrogen containing organic compounds, etc.)
NO₃ saturation anywhere in the basin is cause for alarm because it can eventually result in an increase of ozone concentrations around the well-mixed basin, which will serve only to exacerbate the current air pollution problems that stem from the transport of ozone rich air from Sacramento.

Further increases in local NO production will need to be avoided if Lake Tahoe is to maintain its current status as primarily VOC sensitive. If the NO production in the basin increases to the point where a large portion of Lake Tahoe becomes a VOC sensitive regime, Ozone levels will peak (when the ratio becomes 5.5:1 VOC:NO2) that is, the highest possible rate of ozone production for the coinciding VOC concentration will be observed. Past this point any additional NO₂ will lead to increased titration of the hydroxyl radical and actually a decrease in ozone production. Decreasing the NO levels will initially bring Lake Tahoe back into the range of peak ozone formation before NOₓ sensitivity can be regained.

**Consequences of Titration (NO₂ and OH radical)**

Increased NO₂ and hydroxyl radical titration is not preferred as the product (nitric acid) will likely be deposited into the lake. This process will result in an increase in algae and ultimately a greener, less clear lake. If Lake Tahoe is to be “kept blue”, then nitric oxide concentrations will need to be kept low.

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Conclusions:

Most of the ozone measured in the Lake Tahoe Basin had been transported in by air parcels that had travelled through the Sacramento Valley. One region of the basin (that surrounding the TRPA site) showed signs of a transition from NOx sensitivity to VOC sensitivity. While Lake Tahoe is not yet in immediate danger of becoming a notoriously polluted area the situation is indeed growing more serious. Lake Tahoe will not remain pristine if:

A. Local production of nitric oxide, and thereby ozone, increases and VOC sensitivity is attained

B. Transport of ozone and ozone precursors, from areas outside of the Tahoe Basin, increases

Further Research

Researchers at the Dessert Research Institute are currently analyzing data for ambient concentrations of volatile organic compounds in the basin. These data will be used to determine a more exact number for the optimal VOC:NO$_2$ ratio for ozone production as not all volatile organic compounds are equally reactive. Further, the CAMX three dimensional model will be implemented in order to gain insight into the chemical transport and chemical reactions that are occurring in the basin.
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References


