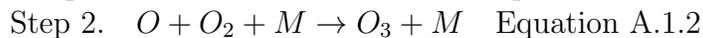


Appendix A
Important Chemical Reactions

Appendix A has been dedicated to delineating all of the important chemical reactions discussed in the paper

1 Important Chemical Reactions For the Formation and Destruction of Ozone

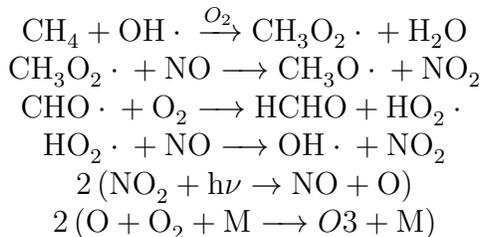
Photolysis of NO_2 to give O_3 a two step process



Ozone can be titrated with nitric oxide according to the following reaction

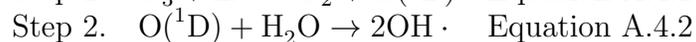
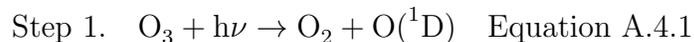


Below is an example of a free radical chain reaction initiated by the interaction between a hydroxyl radical and methane



1.1 The Hydroxyl Radical

Below are the chemical equations representing the formation of the hydroxyl radical needed to initiate the chain reaction that efficiently produces ozone



*note that $\text{O}({}^1\text{D})$ (singlet D oxygen) is atomic oxygen in an excited state

1.2 The Hydroxyl Radical and The VOC: NO_2 ratio

On average the hydroxyl radical reacts 5.5 times faster with NO_2 than it does with the typical volatile organic compound.

That is to say:

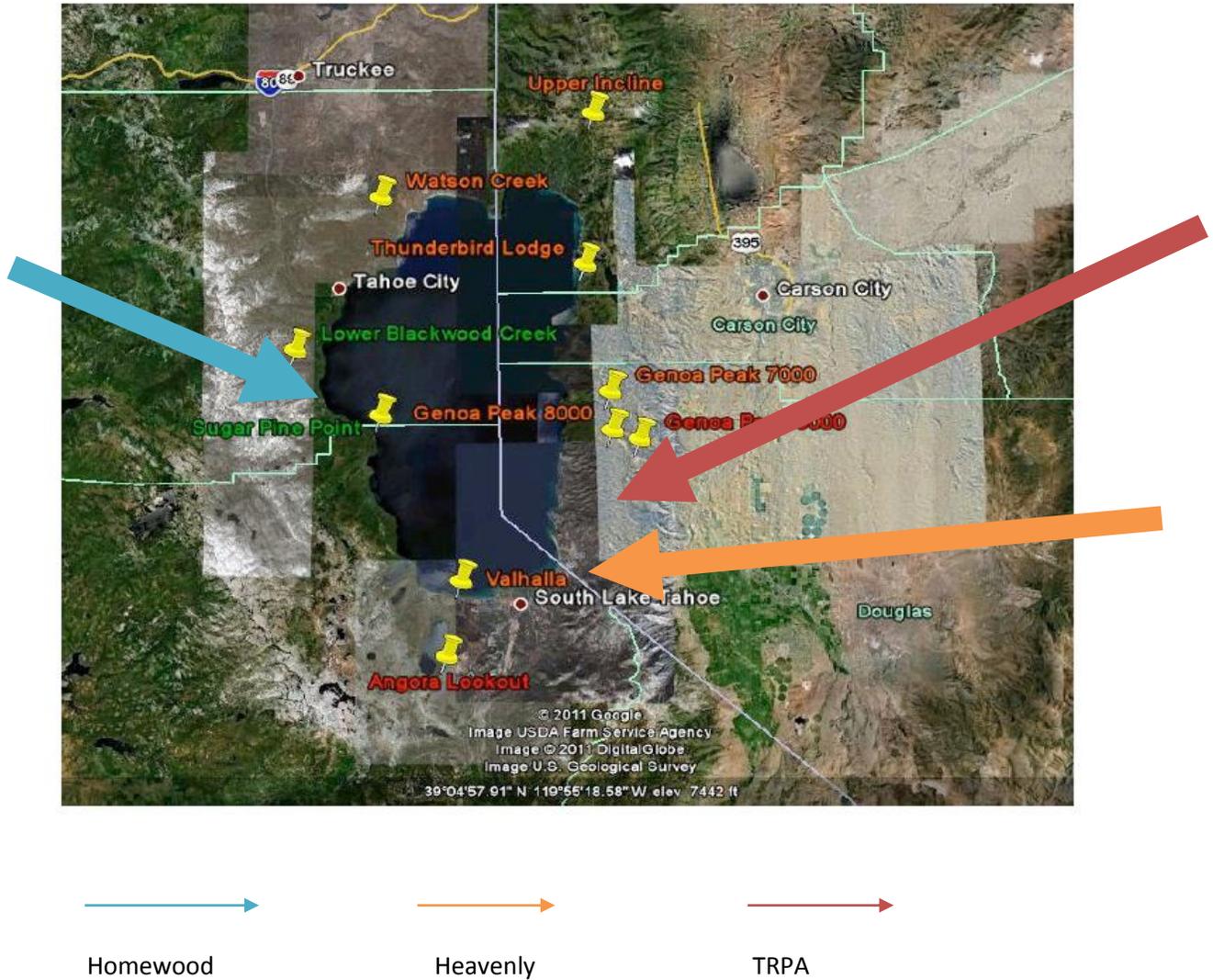
$$k_{\text{NO}_2} : k_{\text{voc}} \approx 5.5$$

where k_{NO_2} and k_{voc} are the rate constants for the reactions between:

1. the hydroxyl radical and nitrogen dioxide and
2. the hydroxyl radical and an average volatile organic compound, respectively

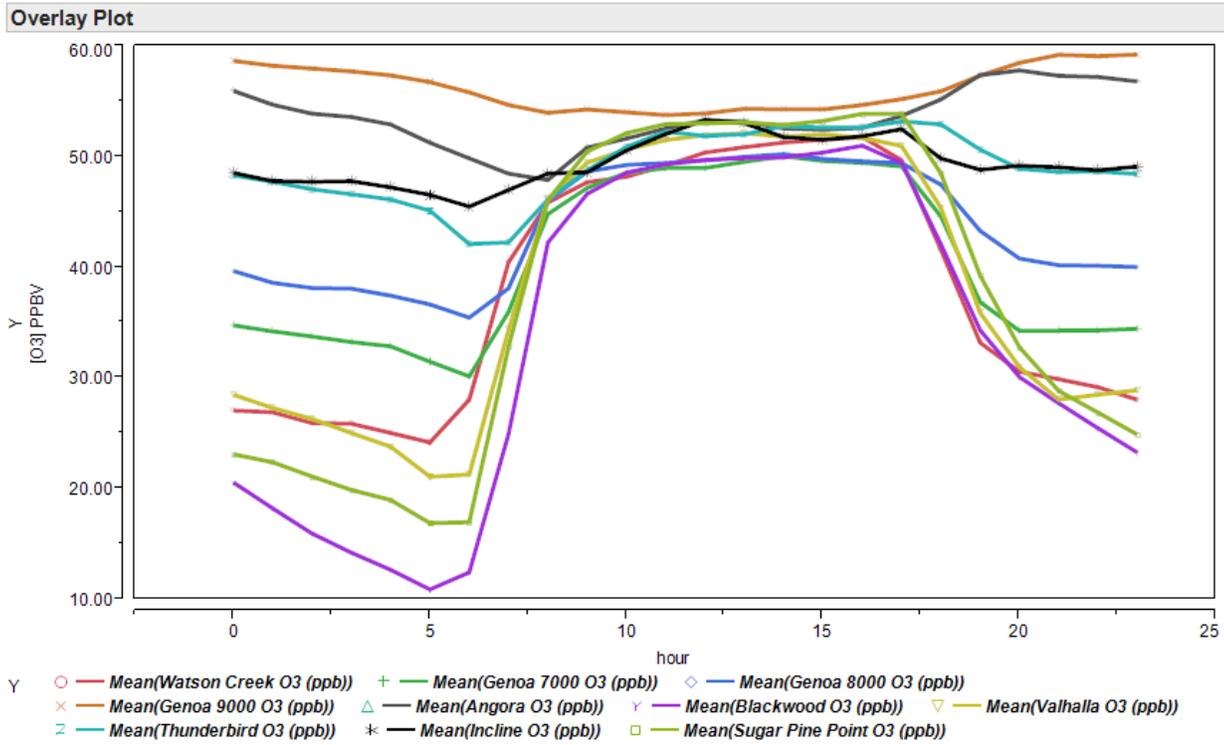
Appendix B

Figure B.1: Map Of Lake Tahoe Showing Each of the Collection Sites for 2010 and 2012



Above: Map of relevant locations around the Tahoe Basin.

Figure B.2 Lake Tahoe Ozone Data 2010 Diurnal Representation

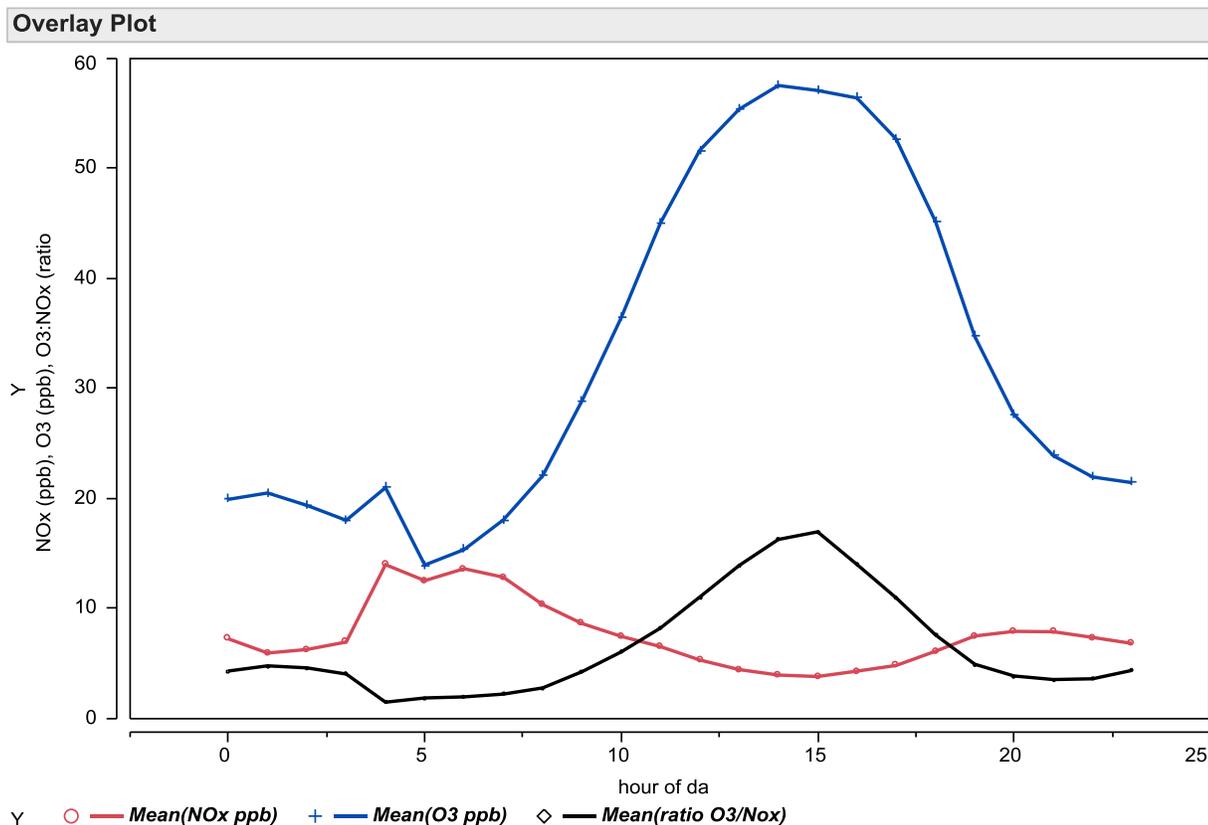


Above: Plot representing average diurnal trends in ozone concentrations around the basin.

Air Quality Data from Areas Other Than Lake Tahoe

Part I

Figure E.1: T Street, Sacramento (VOC sensitive)



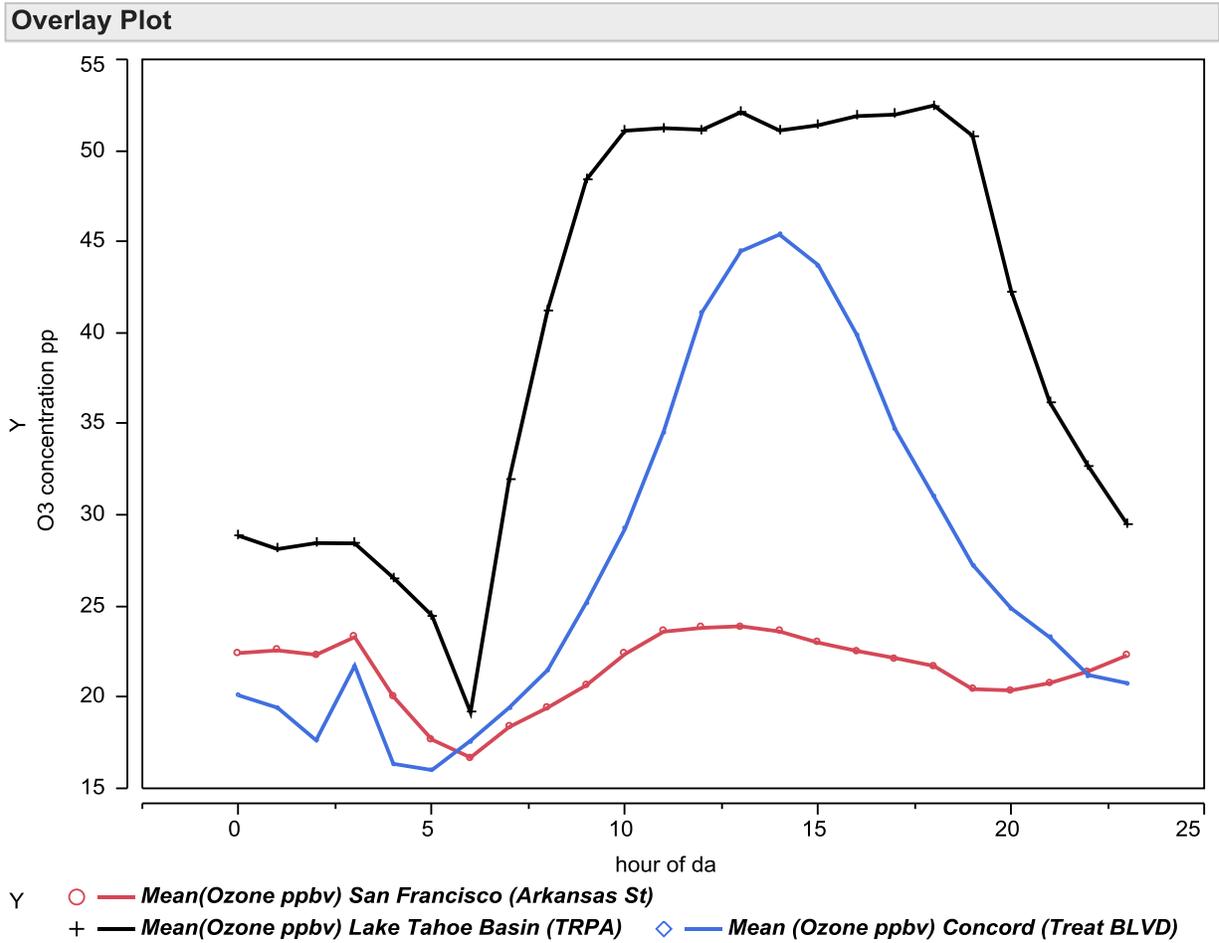
Above: Plot depicting the average diurnal trend for ozone, oxides of nitrogen and the respective ratio between them for the month of July 2012. Note: According to back trajectories acquired through use of the Hysplit model, Sacramento is a major source of the ozone rich air in the Lake Tahoe Basin.

Compare the plot above, with a midday maximum ozone concentration of approximately 57 ppbv, to the diurnal ozone concentration plot for the Lake Tahoe study, consisting of a midday maximum ozone concentration of approximately 55 ppbv.

PART II : Data Comparison

The following plot gives a direct comparison between San Francisco (Arkansas Street), Concord (Treat Boulevard), and Lake Tahoe (TRPA). The CARB sites represented in the plot below are not necessarily related, in any way, to air quality in Lake Tahoe (that is, by trajectory of air parcels). They are simply meant to contextualize the Lake Tahoe data.

Figure E.2: Comparison Plot



Above: diurnal plot comparing average ozone concentrations in Lake Tahoe, San Francisco Ca, and Concord Ca for the month of July 2012.

Appendix C

Appendix D: Ozone Monitor Theory of Operation

1. OZONE MONITOR INTRODUCTION

The 2B Technologies Ozone Monitor is designed to enable accurate measurements of atmospheric ozone over a wide dynamic range extending from a limit of detection of 1.5 parts-per-billion by volume (ppbv) to an upper limit of 100 parts-per-million (ppmv) based on the well established technique of absorption of ultraviolet light at 254 nm. The Ozone Monitor is light weight (4.7 lb., 2.1 kg.) and has a low power consumption (\approx 4 watt) relative to conventional instruments and is therefore well suited for applications such as:

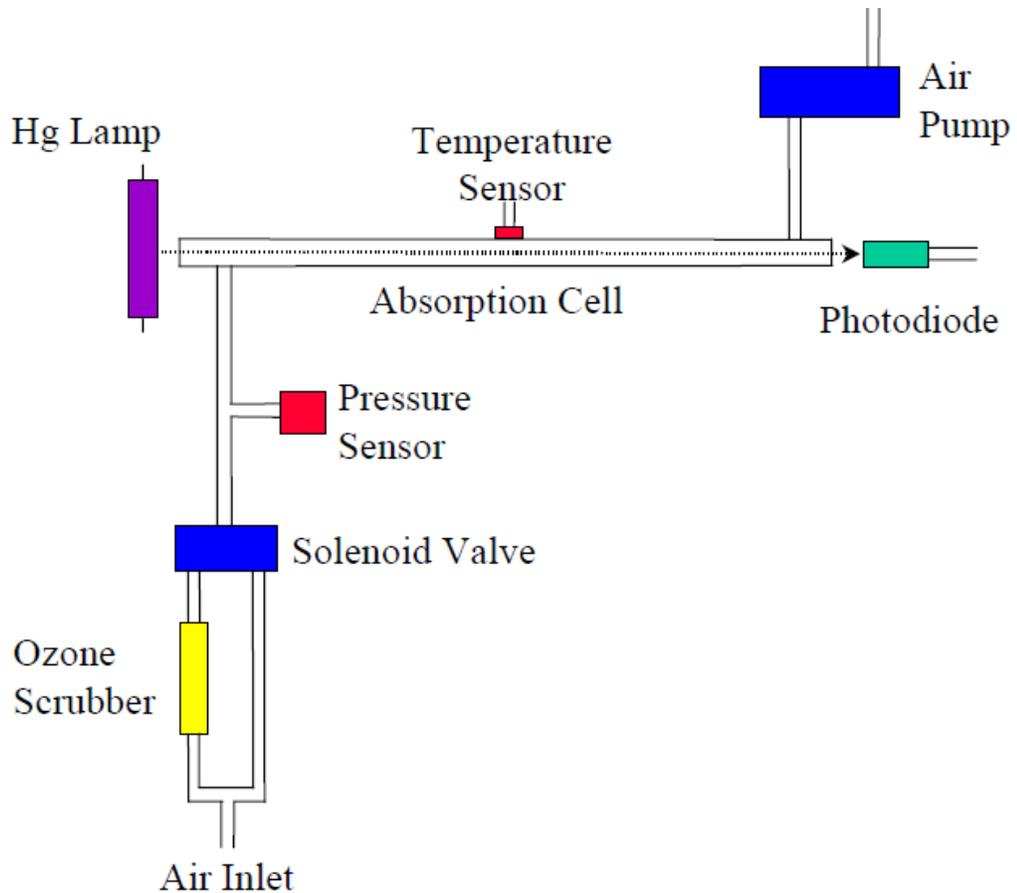
- vertical profiling using balloons, kites, remotely piloted aircraft, and other aircraft where space and weight are highly limited
- long-term monitoring at remote locations where power is highly limited
- urban arrays of ground-based detectors
- personal exposure monitoring for studies of health effects of air pollutants

Theory of Operation

Absorption of UV light has long been used for measurements of atmospheric ozone with high precision and accuracy. The ozone molecule has an absorption maximum at 254 nm, coincident with the principal emission wavelength of a low-pressure mercury lamp. Fortunately, few molecules found at significant concentrations in the atmosphere absorb at this wavelength. However, interferences, such as organic compounds containing aromatic rings, can occur in highly polluted air.

Figure 1 is a schematic diagram of the ozone monitor. Ozone is measured based on the attenuation of light passing through a 15-cm long absorption cell fitted with quartz windows. A low-pressure mercury lamp is located on one side of the absorption cell, and a photodiode is located on the opposite side of the absorption cell. The photodiode has a built-in interference filter centered on 254 nm, the principal wavelength of light emitted by the mercury lamp. An air pump draws sample air into the instrument at a flow rate of approximately 1 L/min. A solenoid valve switches so as to alternately send this air directly into the absorption cell or through an ozone scrubber and then into the absorption cell. The intensity of light at the photodiode is measured in air that has passed

Figure D.1: Schematic Diagram of Ozone Monitor



through the ozone scrubber (I_o) and air that has not passed through the scrubber (I). Ozone concentration is calculated from the measurements of I_o and I according to the Beer-Lambert Law:

$$C_{O_3} = \frac{1}{\sigma l} \ln\left(\frac{I_o}{I}\right) \quad \text{Equation D.1}$$

where l is the path length (15 cm) and σ is the absorption cross section for ozone at 254 nm ($1.15 \times 10^{-17} \text{ cm}^2 \text{ molecule}^{-1}$ or $308 \text{ atm}^{-1} \text{ cm}^{-1}$), which is known with an accuracy of approximately 1%. The 2B Technologies instrument uses the same absorption cross section (extinction coefficient) as used in other commercial instruments.

The logarithm of equation 1 is approximated in the microprocessor of the instrument with sufficient accuracy to provide five orders of dynamic range; ozone mixing ratios are measured up to 100 ppmv, as compared to 1 ppmv for most commercial ozone instruments.

The pressure and temperature within the absorption cell are measured so that the ozone concentration can be expressed as a mixing ratio in parts-per-billion by volume (ppbv). The instrument displays and records the cell temperature and pressure in addition to the ozone mixing ratio. The cell pressure is displayed and logged in units of either Torr or mbar and the cell temperature in units of either °C or K.

In principle, the measurement of ozone by UV absorption requires no external calibration; it is an absolute method. However, non-linearity of the photodiode response and electronics can result in a small measurement error. Therefore, each instrument is compared with a NIST-traceable standard ozone spectrophotometer in the laboratory over a wide range of ozone mixing ratios. These results are used to calibrate the Ozone Monitor with respect to an offset and slope (gain or sensitivity). The corrections for offset and slope are recorded in the instrument Birth Certificate and on a calibration sticker that can be viewed by removing the top cover of the instrument. These calibration parameters are entered into the microprocessor prior to shipment. The user may change the calibration parameters from the front panel if desired. It is recommended that the instrument be recalibrated at least once every year and preferably more frequently. The offset may drift due to temperature change or chemical contamination of the absorption cell. As discussed below, an accurate offset correction can be measured from time to time using the ozone scrubber supplied with the instrument.

Appendix E

Observation Based Methods (Developed by Sanford Sillman)

Table 2.2. Values of indicator ratios for NO_x-sensitive, transitional, and VOC-sensitive conditions

The VOC-sensitive and NO_x-sensitive values represent typical values for strongly VOC-sensitive and strongly NO_x--sensitive locations, derived from chemistry/transport models. Ratios lower than the transition values generally correspond to VOC-sensitive conditions. Ratios higher than the transition values generally correspond to NO_x-sensitive conditions.

Indicator	Median VOC-Sensitive	Transition	Median NO_x-Sensitive
O₃/NO_y	5	6-8	11
O ₃ /NO _z	6	8-10	14
O ₃ /HNO ₃	9	12-15	20
(O ₃ -O _{3b})/(NO _y -NO _{yb})	3	3.5-5	6
(O ₃ -O _{3b})/(NO _z -NO _{zb})	4	5-6	7
(O ₃ -O _{3b})/(HNO ₃ -HNO _{3b})	5	7-10	12
H ₂ O ₂ /HNO ₂	.15	.25-.35	.6
Total peroxides/HNO ₃	.2	.2-.5.	9
H ₂ O ₂ /NO _z	.12	.2-.25	.4
Total peroxides/NO _z	.15	.25-.35	.7
H ₂ O ₂ /NO _y	.08	.12-.17	.35
Total peroxides/NO _y	.12	.20-.25	.6