OVERVIEW: TROPOSPHERIC OZONE, SMOG AND OZONE-NO_x-VOC SENSITIVITY.

Dr. Sanford Sillman
Research Scientist
University of Michigan
sillman@umich.edu
http://www-personal.engin.umich.edu/~sillman

Also available: a report on observation-based methods for analyzing ozone-NO_x-VOC sensitivity, and Dr. Sillman's published journal articles. (Go to http://www-personal.engin.umich.edu/~sillman).

For more complete information, along with references for work cited here:

Sillman, S., Tropospheric ozone and photochemical smog, in B. Sherwood Lollar, ed., Treatise on Geochemistry, Vol. 9: Environmental Geochemistry, Ch. 11, Elsevier, 2003. http://www.TreatiseOnGeochemistry.com ***.For availability, contact the author.***

Sillman, S., The relation between ozone, NO_x and hydrocarbons in urban and polluted rural environments. Millenial Review series, Atmos. Environ., 33, 12, 1821-1845, 1999. (Available at http://www-personal.engin.umich.edu/~sillman).

Additional resource: The NARSTO web site (http://www.cgenv.com/Narsto) contains comprehensive reviews of ozone and particulates.

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1.1. What is ozone?

Ozone (O_3) is the primary ingredient of **photochemical smog**, the type of air pollution that is associated with sunlight-driven chemical reactions. Ozone is associated in particular with the type of air pollution events that occur in Los Angeles and Mexico City, often associated with automobile emissions.

Ozone itself is colorless and invisible, but often occurs along with other, more visible species (e.g. sulfate aerosols) in large-scale pollution events.

Ozone is a pollutant of concern because it is associated with extensive **health effects**, most notably associated with the respiratory system. Ozone is also a pollutant of concern because it can affect both **forests** and **agricultural crops**. Ozone levels in urban areas during pollution events are believed to be high enough to affect human health. Many metropolitan areas in the U.S. are currently (2003) in violation of government health standards for ozone, and violations of health standards have been occurring since the standards were first established in the 1970's.

Pollution events with high ozone are associated specifically with sunshine and warm temperatures. High ozone is very rare when temperatures are below 20 C (68 F), and are usually associated with temperatures above 30 C (86 F). High ozone is also associated with relatively light winds and conditions that suppress vertical mixing in the atmosphere (thermal inversions or subsidence layers), but the most important conditions are sunshine and high temperatures.

Pollution events are not limited to cities. Typically, the highest ozone levels are found in suburban locations downwind from the city center, rather than in the city center itself. In some situations plumes with high ozone have been found in locations that are 500 km (300 mi) distant from the apparent emission sources. In addition, densely populated regions are subject to pollution events with uniformly high ozone, affecting both urban and rural areas. During these regional pollution events, elevated ozone may extend over an area as large as 1000x1000 km (600x600 mi). Events of this type have occurred in the eastern U.S., California and in western Europe (see **Figure 1.1**).

Ozone as an air pollutant should not be confused with the **ozone layer** in the stratosphere. Ozone occurs naturally in the stratosphere – the atmospheric layer located between 20 and 60 km (15 and 40 miles) above the earth's surface. Ozone levels in the stratosphere are 50 times higher than in the most polluted city – but no one has to breathe that air. Stratospheric ozone is beneficial to life on earth, because it blocks harmful ultraviolet radiation. Over the past 50 years human activities have caused a 5% decrease in the amount of stratospheric ozone and in particular have lead to the occurrence of an **ozone hole** over Antarctica during the southern hemisphere spring. This damage to the ozone layer was primarily the result of **chlorofluorocarbons (CFCs)**, which accumulate in the atmosphere and eventually affect the ozone layer. The **Montreal Protocol (1987)** planned for the reduction and eventual worldwide ban on the production of CFC's. None of this relates to ozone as an air pollutant.

Ozone also occurs naturally at the earth's surface, due in part to transport downward from the ozone layer in the stratosphere and in part to naturally occurring chemistry in the lower atmosphere (the troposphere). However, ozone during pollution events is approximately ten times the natural level. In addition, human activities have caused an increase in ozone at the global scale, especially in the northern hemisphere. Thus, even the most remote locations in the northern hemisphere have significantly more ozone than would occur naturally.

Ozone levels are typically expressed in **parts per billion by volume (ppbV, or ppb)**, which represent the fraction of air molecules represented by ozone. The following are typical ozone levels (mixing ratios):

Natural background (pre-industrial):	10-20 ppb
Remote locations in the Northern Hemisphere:	20-40 ppb (varying by season and latitude)
Rural areas during region-wide pollution events	80-100 ppb
Peak O_3 in urban areas during pollution events	120-200 ppb
Maximum urban O_3 (Los Angeles, Mexico City)	490 ppb
Stratospheric ozone layer	15000 ppb
USEPA health standard for ozone	125 ppb, 1-hour exposure
(proposed revision:	85 ppb, 8 hour exposure)

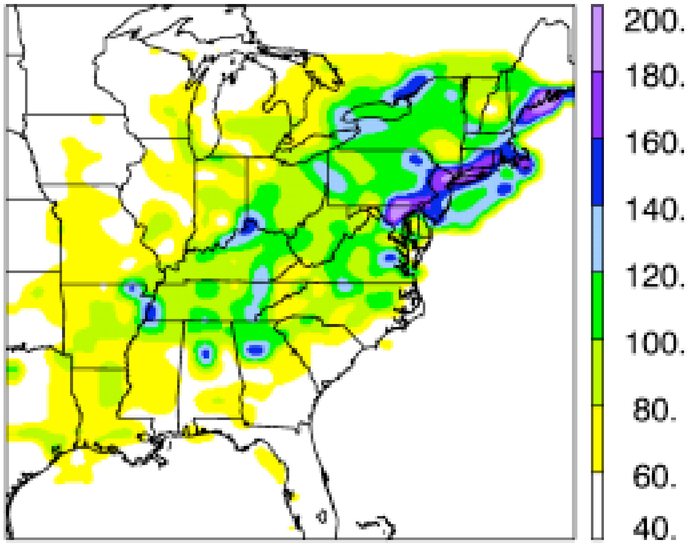

Figure 1.1. Extent of an air pollution event. The figure shows peak ozone in the eastern U.S. on June 15, 1988 based on surface observations at 350 EPA monitoring sites. Ozone above 80 ppb extends continuously from Tennessee to Maine. The ozone plume from New York City and Boston extends to Cape Cod and along the coast of Maine. First printed in Sillman (1993).

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1.2. Ozone, NO_x and VOC.

1.2.1. Ozone formation is driven by two major classes of directly emitted precursors: nitrogen oxides (NO_x) and volatile organic compounds (VOC). The relation between O_3, NO_x and VOC is driven by complex nonlinear photochemistry.

The relation between O_3, NO_x and VOC can be illustrated by isopleth plots (**Figure 1.2**), which shows peak O_3 during the afternoon as a function of NO_x and VOC mixing ratios or (as shown here) emission rates. As shown in the figure, it is possible to identify two regimes with different O_3-NO_x-VOC sensitivity. In the **NO_x-sensitive** regime (with relatively low NO_x and high VOC), O_3 increases with increasing NO_x and changes little in response to increasing VOC. In the **NO_x-saturated** or **VOC-sensitive** regime O_3 decreases with increasing NO_x and increases with increasing VOC. The dotted line (the **ridge line**) represents a local maximum for O_3 versus NO_x and VOC, separates the NO_x-sensitive and VOC-sensitive regimes.

The response of ambient O_x to reductions in emissions of NO_x and VOC is also shown in results for indicator ratios, elsewhere in this site.

WARNING: The exact dependence of O_3 on NO_x and VOC in isopleth plots varies greatly depending on assumptions and conditions used in generating the isopleth plot. The pattern (with a split into NO_x-sensitive and NO_x-saturated regimes) tends to recur for a wide range of conditions, but the values of VOC and NO_x associated with the transition between regimes change.

Ambient NO_x and VOC mixing ratios are directly related to the instantaneous rate of production of O_3, and it may be possible to make inferences about the instantaneous production rate of O_x based on ambient NO_x and VOC. A more robust form of the isopleth plot can be created by plotting the instantaneous rate of production of O_3 versus summed ambient VOC and NO_x, where the VOC sum is weighted by reactivity. This is discussed in the report on Observation-based Methods Section 4, elsewhere at this site.

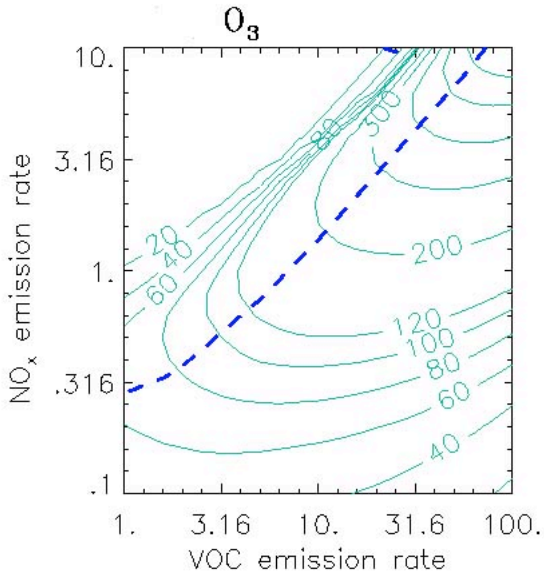


Figure 1.2. Ozone isopleths (ppb) as a function of the average emission rate for NO_X and VOC (10^{12} molec. cm^{-2} s^{-1}) in 0-d calculations. The isopleths (solid green lines) represent conditions during the afternoon following 3-day calculations with a constant emission rate, at the hour corresponding to maximum O_3. The short blue dashed line represents the transition from VOC-sensitive to NO_X-sensitive conditions.

1.2.2. Factors affecting O_3-NO_x-VOC sensitivity.

O_3-NO_x-VOC sensitivity for individual locations and events are often very uncertain (see 1.2.3. below). Generalizations about NO_x-sensitive versus VOC-sensitive conditions are always very approximate and subject to many exceptions. The following are offered as broad guidelines for understanding the factors that cause O_3-NO_x-VOC sensitivity to vary for different locations and for different events.

- ***VOC/NO_x ratio***. NO_x-sensitive conditions are associated with high VOC/NO_x ratios and VOC-sensitive conditions are associated with low VOC/NO_x ratios (see **Figure 1.1**).

  WARNING: VOC/NO_x ratios are associated with the instantaneous production rate of O_3, not necessarily the ambient O_3 mixing ratio. Ambient O_3 is the result of photochemistry and transport over several hours (and often several days), and ambient VOC and NO_x can vary greatly over time and through the upwind region in which the ozone was produced.

- ***VOC reactivity***. A more reactive VOC mix is associated with NO_x-sensitive conditions. The split between NO_x-sensitive and VOC-sensitive conditions is correlated with the ratio of reactivity-weighted VOC to NO_x, rather than the ratio of the simple sum of VOC to NO_x (see report on Observation-based methods).

- ***Biogenic VOC***. Naturally occurring VOC (especially isoprene, emitted primarily by oaks and other deciduous trees) represents a significant fraction of total ambient VOC, especially in suburban and rural settings and when VOC is weighted by reactivity. Biogenic VOC is especially important because they are usually highly reactive. Biogenic NO_x is far smaller relative to the anthropogenic source. A high rate of biogenic VOC increases the ratio of reactivity-weighted VOC to NO_x and makes NO_x-sensitive conditions more likely. (Chameides et al., 1988, 1992; Pierce et al., 1998).

- ***Downwind distance***. As air moves downwind from emission sources and ages photochemically, conditions tend to change from VOC-sensitive (closer to emission sources) to NO_x-sensitive (further from emission sources). This occurs because NO_x is removed more rapidly than VOC as an air mass moves downwind (thus increasing the VOC/NO_x ratio) and because biogenic VOC becomes increasingly important as air moves downwind (Milford et al., 1989, 1994).

  WARNING: There are likely to be many exceptions to this rule. NO_x-sensitive conditions are possible even in an urban center, and VOC-sensitive conditions can occur even at far downwind locations (Jacob et al., 1995; Kleinman et al., 2000)

1.2.3. Uncertainty in O_3-NO_x-VOC sensitivity predictions.

The split between NO_x-sensitive and VOC-sensitive chemistry is a major source of uncertainty in predictions for the relation between O_3 and precursor emissions.

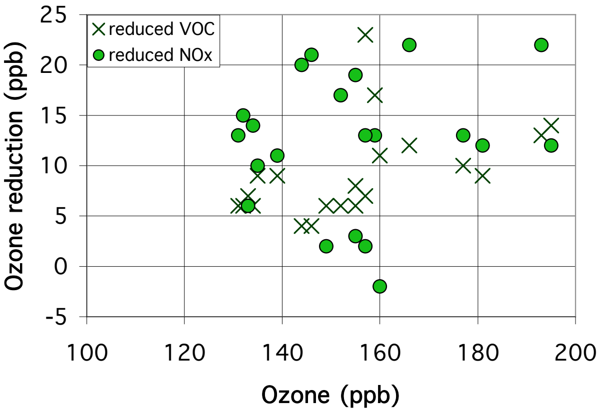
NO_x-VOC sensitivity is difficult to predict, and there are no simple "rules of thumb" for distinguishing NO_x-sensitive from VOC-sensitive conditions. O_3-precursor sensitivity predictions are usually derived from 3-dimensional Eulerian chemistry/transport models. These models are subject to many uncertainties that affect their ability to identify NO_x-sensitive vs. VOC-sensitive conditions. Different assumptions in models may lead to very different results for predicted sensitivity to NO_x and VOC.

Emission inventories are often the largest source of uncertainty in model sensitivity predictions. O_3-precursor sensitivity depends critically on emission rates for anthropogenic VOC and NO_x, on the speciation of anthropogenic VOC, and on emission rates for biogenic VOC.

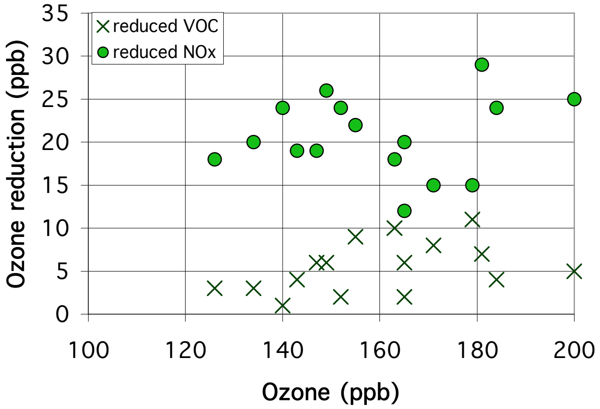
Evaluation of chemistry/transport models is usually based on the ability of the model to predict O_3 in comparison with ambient measurements. However, success in simulating the observed O_x does not guarantee that models predict the O_3-NO_x-VOC sensitivity correctly. Frequently it is possible to create different model scenarios for an event that give similar O_3 but with very different predictions for NO_x-VOC sensitivity (Sillman et al., 1995, Reynolds et al., 1996, Pierce et al., 1998).

Effect of uncertainty. **Figure 1.3** illustrates the uncertainty in predictions for the impact of reduced NO_x and VOC. The figures show the reduction in peak O_3 resulting from reduced NO_x and VOC, as predicted by a series of different model scenarios for two days in Atlanta. On the first day, a 35% reduction in NO_x emissions is predicted to cause changes in peak O_3 ranging from a 23 ppb decrease to a 2 ppb increase, depending on which model scenario is chosen. Similarly, a 35% reduction in anthropogenic VOC is predicted to cause changes in peak O_3 ranging from a 23 ppb reduction to a 2 ppb reduction. This range of uncertainty occurs because the model chemistry may be predominantly NO_x-sensitive or predominantly VOC-sensitive, depending on assumptions about emission rates and meteorology. Uncertainties are less on the second day (12-29 ppb reduction in O_3 for reduced NO_x; 0-11 ppb reduction for reduced VOC) because model uncertainties do not cause a switch from NOx-sensitive to VOC-sensitive chemistry.

Observation-based methods (OBMs) can be used to reduce the uncertainty in predictions for the impact of reduced NO_x and VOC on O_3. OBMs may provide an independent observation-based estimate for the relative impact of NO_x and VOC. The most important use of OBMs is to provide an observation-based evaluation and constraint on chemistry/transport models, in order to reduce the uncertainty in NO_x-VOC predictions shown in **Figure 1.3**.



(a) August 10, 1992



(b) August 11, 1992

Figure 1.3. Impact of model uncertainty on control strategy predictions for O3 for two days in Atlanta, GA. The figures show the predicted reduction in peak O_3 resulting from 35% reductions in anthropogenic VOC emissions (crosses) and from 35% reductions in NO_x (solid circles) in a series of model scenarios with varying base case emissions, wind fields and mixed layer heights. Results are plotted from tabulated values published in Sillman et al. (1995, 1997).

1.3. Chemistry of ozone and cause of the NOx-VOC split.

Ozone formation occurs through the following sequence of reactions. The sequence is almost always initiated by the reaction of various VOC or CO with the OH radical **[R1, R2]**. This is followed by the conversion of NO to NO_2 (through reaction with HO_2 or RO_2 radicals), which also regenerates OH **[R3, R4]**. NO_2 is photolyzed to generate atomic oxygen, which combines with O_2 to create O_3 **[R5, R6]**.

$$\mathrm{VOC + OH \xrightarrow{[O2]} RO_2 + H_2O} \qquad \text{R1}$$

$$\mathrm{CO + OH \xrightarrow{[O2]} HO_2 + CO_2} \qquad \text{R2}$$

$$\mathrm{RO_2 + NO \xrightarrow{[O2]} secondary\ VOC + HO_2 + NO_2} \qquad \text{R3}$$

$$\mathrm{HO_2 + NO \rightarrow OH + NO_2} \qquad \text{R4}$$

$$\mathrm{NO_2 + h\nu \rightarrow NO + O} \qquad \text{R5}$$

$$\mathrm{O + O_2 + M \rightarrow O_3 + M} \qquad \text{R6}$$

Here, RO_2 represents any of a number of chains of organics with an O_2 attached (replacing H in the original chain). For example: propane (C_3H_8) reacts with OH **[R1]** to generate the following RO_2: $C_2H_7O_2$. This reacts with NO **[R3]** to generate C_2H_5CHO (propionaldehyde) and H (which combines with O_2 to form HO_2).

The **rate of ozone formation** is controlled primarily by the rate of the initial reaction of VOC with OH.

NO_x titration: Elevated ozone in polluted regions is usually due to the ozone production sequence shown above. However, at nighttime and in the immediate vicinity of very large emissions of NO (e.g. power plants), ozone concentrations are depressed through the process of NO_x titration. This consists of the removal of O_3 through reaction with NO **[R7]**.

$$NO+O_3 \rightarrow NO_2+O_2 \qquad R7$$

During the daytime, this reaction is normally balanced by the photolysis of NO_2 **[R5, R6]**. However, in the vicinity of large NO emissions the result is net conversion of O_3 to NO_2. This is most common in the vicinity of large point sources. Ozone is depressed immediately downwind of these sources, and becomes elevated as the plume moves further downwind (Gillani et al., 1996).

At nighttime, there is no photolysis of NO_2 reaction **R7** also leads to the removal of ozone.

NO_x-sensitive vs NO_x-saturated: The split between NO_x-sensitive and NO_x-saturated regimes, illustrated in **Figure 1.2**, is driven by the chemistry of odd hydrogen radicals. There are two main sinks for these radicals: **peroxide**s and **nitric acid** (HNO_3). When peroxides represent the dominant radical sink, chemistry is NO_x-sensitive. when HNO_3 represents the dominant sink, conditions are NO_x-saturated. This is described in more detail immediately below.

Odd hydrogen radicals consist of OH, HO_2 and species with the form RO_2. This family is directly connected to the chemistry of ozone production, because the initial reaction of the ozone production sequence (VOC+OH, **R1**) is driven by OH and subsequent steps depend on HO_2 and RO_2. The ozone production rates depend on the abundance of OH, which depends on sources and sinks of odd hydrogen radicals as a whole.

Radical **sources** include photolysis of ozone, formaldehyde, and other secondary VOC.

$$O_3 + h\nu \xrightarrow{[H_2O]} 2OH + O_2 \qquad R8$$

$$HCHO + h\nu \xrightarrow{2O_2} 2HO_2 + CO \qquad R9$$

Radical **sinks** include formation of hydrogen peroxide (**R10**) and organic peroxides (**R11**) , formation of nitric acid (**R12**) and net formation of peroxyacetyl nitrate and other organic nitrates.

$$HO_2 + HO_2 \rightarrow H_2O_2 + O_2 \qquad R10$$

$$RO_2 + HO_2 \rightarrow ROOH + O_2 \qquad R11$$

$$OH + NO_2 \rightarrow HNO_3 \qquad R12$$

NO_x-sensitive regime occurs when peroxides (**R10** and **R11**) represent the dominant radical sink. In this case, ambient concentrations of HO_2 and RO_2 radicals will be determined by the balance between radical sources (**R8** and **R9**) and the peroxide-forming reactions (**R10** and **R11**). Because the rate of peroxide formation is quadratic in HO_2, the ambient concentrations of HO_2 and RO_2 show little variation in response to changes in NO_x and VOC. The rate of ozone formation is determined by the reaction of HO_2 and RO_2 with NO (**R3** and **R4**). This rate increases with increasing NO_x. In polluted regions the rate of ozone formation usually is relatively unaffected by changes in VOC. In remote regions the rate of ozone formation also increases with increasing VOC.

NO_x –saturated (VOC-sensitive) regime occurs when nitric acid (**R12**) represents the dominant radical sink. In this case, ambient concentrations of OH will be determined by the balance between radical sources (**R8** and **R9**) and the reaction of OH with NO_2 (**R12**). Because the rate of nitric acid formation (**R12**) increases with NO_2, ambient OH decreases with increasing NO_2. The rate of ozone formation is determined by the rate of the reaction of VOC and CO with OH (**R1** and **R2**). This rate increases with increasing VOC and decreases with increasing NO_x.

VOC/NO_x ratios: The split between NO_x sensitive and VOC-sensitive regimes is closely related to the ratio of summed VOC to NO_2, assuming that the sums are weighted by reactivity (rVOC/NO_2).

The formation rate of ozone and the radical source term **[R9]** both increase with increases in the rate of the reaction of VOC with OH **[R1]**.

The rate of formation of nitric acid, a critical radical sink, depends on the rate of the reaction of NO_2 with OH **[R12]**.

The ratio of radical sources to the formation rate of nitric acid (as a radical sink) is proportional to the ratio of summed VOC (weighted by reactivity with OH] to NO_2. When this ratio is high, peroxides become the dominant radical sink and conditions are NO_x-sensitive. When this ratio is low, nitric acid becomes the dominant radical sink and conditions are NO_x-saturated.

WARNING: VOC/NO_x ratios are associated with the instantaneous production rate of O_3, not necessarily the ambient O_3 mixing ratio. Ambient O_3 is the result of photochemistry and transport over several hours (and often several days), and ambient VOC and NO_x can vary greatly over time and through the upwind region in which the ozone was produced.

Ozone production efficiency per NO_x is equal to the ratio of the rate of ozone formation to the rate of removal of NO_x (largely by chemical conversion to HNO_3). The ozone formation rate is proportional to the rate of the reaction of VOC with OH. The conversion of NO_x to nitric acid is proportional to the rate of the reaction of NO_2 with OH. The ozone production efficiency is equal to the ratio of these rates. Therefore, it is also related to the ratio of summed VOC(weighted by reactivity with OH) to NO_2.

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