

Natural Sources of Ozone: Their Origin
and Their Effect on Air Quality

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INTRODUCTION

The National Ambient Air Quality Standard for ozone is being violated in many urban and rural areas of the U.S. Cities and states which violate the standard must submit plans for meeting it. Since controlling emissions for ozone reduction is a costly endeavor, any possibility that violations occur due to natural causes is a very important consideration.

This report deals with the major natural sources of ozone in the atmosphere, and tries to explain how they compare and interact with anthropogenic, (man-made) sources. The two main natural sources of ozone are: 1) the stratosphere, which provides ozone to the troposphere through various physical transport mechanisms and 2) biogenic hydrocarbons, (from plants and trees) which react in sunlight with nitrogen oxides to form ozone. In comparison to these sources, other natural sources, such as lightning, of atmospheric ozone are negligible, so this report will focus on these two sources only.

On the average, natural sources of ozone contribute an ambient background (non-man-made) level of about 0.02 - 0.05 ppm (parts per million). The actual level for a particular site depends on many factors, such as geography and climate.

The National Ambient Air Quality Standard for ozone is a one-hour standard of 0.12 ppm (multiple exceedances in a single day count as one, however), so it is clear that man-made sources must contribute most of the ozone in places where the standard is being violated. The concern in this paper, however, is whether occasional peaks of naturally produced ozone could cause ozone standard violations that might not have occurred otherwise.

Most of the background ozone concentration derives from the stratosphere. Therefore, the first natural source of ozone to be discussed will be the stratosphere. The issue of natural hydrocarbons' effect on ozone levels will be analyzed next, and finally the total effect will be examined in light of its impact on air quality.

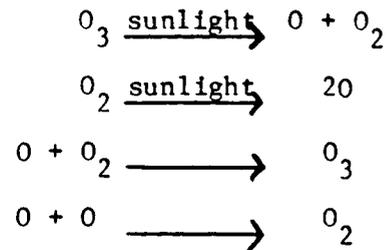
STRATOSPHERIC INTRUSION

Stratospheric Ozone: Background

The stratosphere is the second layer of the atmosphere. It is separated from the troposphere (the layer nearest the earth) by a boundary area called the tropopause, which is about 5-11 miles high (5 miles at the poles, 11 miles above the equator). Warm air from the earth's surface rises in the troposphere, and then gradually sinks again after cooling and contracting. The stratosphere is very stable, and does not contain much air circulation, whereas the troposphere is more active and contains most of the earth's winds.

Ozone is present in both the stratosphere and the troposphere, however, the mechanisms for ozone's formation in these two layers differs. In the stratosphere, ultraviolet light from the sun provides energy to dissociate, or

break apart, molecular oxygen (O_2) into atomic oxygen (O). Atomic oxygen then reacts very quickly with either O_2 to form ozone (O_3), or with more atomic oxygen to reform O_2 , as diagrammed below:



Since O_2 and O_3 are constantly being dissociated, the net reaction produces a steady state concentration of O_3 in the stratosphere.

Stratospheric ozone absorbs ultraviolet light and thus acts as a shield protecting the biosphere below. Life as we know it would not exist without this shield. Ozone from the stratosphere is constantly diffusing into the troposphere, resulting in background levels from this source of about 0.02-0.04 ppm.³ In addition, meteorological factors can cause infrequent, decentralized, larger scale intrusions of ozone from the stratosphere into the troposphere.

Stratospheric ozone in the troposphere is a source of some concern to air quality planners, because of its fluctuations and because it is sometimes difficult to identify as such. The main source of concern is sporadic, larger-scale intrusions of stratospheric ozone (which might contribute to violations of the ozone standard), rather than the more usual, gradual diffusion.

Mechanisms for Ozone Intrusion from the Stratosphere

There are four key mechanisms by which stratospheric ozone enters the troposphere. Two of these processes take place on a world-wide, relatively continuous basis. The other two occur sporadically, and their contribution to ozone concentrations in any given time or place is difficult to ascertain.

The gradual diffusion mechanisms account for almost all of the ambient natural background ozone of stratospheric origin, about 0.02-0.04 ppm.¹ The most important of these processes is called mean meridional circulation. This refers to the mixing of stratospheric and tropospheric air along the polar front, and subsequent horizontal transport to the mid-latitudes. This atmospheric process, though it occurs year-round, is most intense during the winter when storm activity is greatest. The second mechanism, seasonal tropopause adjustment, involves the mixing that results from the seasonal changes in the height of the tropopause boundary. The height of the tropopause varies seasonally due to temperature changes that cause the troposphere to expand and contract. During the spring, as the tropopause rises with the warming of the atmosphere, this process is of most importance to ozone intrusion.

There are also two sporadic intrusion mechanisms, which are by definition short and localized in nature. However, they can result in high ambient ozone concentrations of short duration. Fortunately they occur very rarely, so their impact on average ozone background levels is minimal. The more important of these mechanisms results from the folding over of the tropopause that can occur when weather phenomena arise which involve large exchanges of air between high and low altitudes (i.e., a thunderstorm). They occur mainly at mid-latitudes where polar and tropical air masses meet, and are most frequent during the spring. The other sporadic intrusion mechanism, small-scale eddy transport, is essentially a smaller version of tropopause folding. Although most tropopause folding contributes an insignificant amount to background ozone concentrations, some sporadic intrusions can yield ambient ozone concentrations at ground level of 0.08 ppm or more. Such strong intrusions have been estimated to occur about once a year at particular mid-latitude locations.

Relationships Between Stratospheric Ozone and Ozone of Anthropogenic Origin

Although ozone from these two sources is physically indistinguishable it is possible in most cases to attribute high ambient ozone concentrations to their proper source. This is due to the different conditions under which the two sources prevail. First, stratospheric ozone intrusions of a sporadic nature (which are the only ones likely to result in high ozone levels) occur predominantly during the spring, a season when there is not usually large-scale formation of ozone in the troposphere from anthropogenic pollutants. Ozone formation from tropospheric sources tends to peak in the summer because of its photochemical nature.

Second, high ozone concentrations of stratospheric origin observed at ground level are usually associated with meteorological phenomena such as storms and rapid temperature changes. High concentrations of ozone of anthropogenic origin, on the other hand, are associated with stagnant air and continuous warm temperatures.

Thus, high levels of ozone from both sources usually do not occur simultaneously. Where an ozone violation occurs without a significant increase in anthropogenic pollution, or sunny weather and warm temperatures, one can probably attribute it to stratospheric intrusion, and vice versa. In the unlikely event that these processes are both present, however, it would be difficult to accurately account for the contributions of each process unless sophisticated meteorological or tracer analyses are performed.

The Effect of Stratospheric Intrusion on Ozone Non-Attainment Areas

The possibility of stratospheric intrusion contributing in a major way to an ozone violation is minimal. First, as discussed previously, intrusions resulting in elevated ground-level ozone concentrations are estimated to occur only about once a year, and second, a combination of high anthropogenic and stratospheric ozone levels is even less likely to occur. However, should a situation occur where unusual stratospheric impact is indicated, the EPA allows it to be disregarded for regulatory purposes as long as the

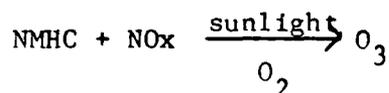
stratospheric intrusion event is documented and supportable.⁴ In addition, one exceedance of the daily standard per year is allowed, so the chance of a non-attainment designation due mainly to stratospheric ozone intrusion is almost nil. Recent studies by Singh, et. al.¹² indicate that at lower U.S. latitudes (below 30°) the threat of summer intrusions affecting ground level ozone concentrations is non-existent.

In summary, although stratospheric ozone is present in the air we breathe, it is not generally a health hazard in and of itself because it is usually present at very low background levels. The main source of ozone levels which are high enough to be unhealthy is anthropogenic in nature. Thus, it is appropriate that air quality planners need to concentrate on the control of man-made ozone precursors, namely hydrocarbons and oxides of nitrogen.

NATURAL HYDROCARBONS:

Ozone Formation

In the lower layer of the atmosphere ozone (O₃) is formed in a series of photochemical reactions where oxygen, non-methane hydrocarbons (NMHC's) and oxides of nitrogen (NOx) combine, as shown in the general equation below:



The rate of formation of ozone in the atmosphere is affected by the relative concentrations of reactants present, the amount of sunlight, the prevailing temperature, and other meteorological conditions. These factors are discussed below.

The relative concentrations of NMHC and NOx are most important. Where the NMHC/NOx ratio is very low or very high, the reaction is inhibited. At very high ratios (greater than 40:1), there is an excess of HC's, and most NMHC's tend to scavenge O₃, NOx, and radicals, thus ending the photochemical reaction chain. At low ratios (less than 4:1), the availability of NMHC becomes the limiting factor. At all times, unreacted NOx can react with O₃, thus acting as an ozone sink (as well as precursor). Smog chamber studies have shown that for the natural hydrocarbons, the maximum ozone is observed at HC/NOx ratios between 10:1 and 20:1;⁵ for anthropogenic hydrocarbons the maximum ozone HC/NOx ratio varies widely with hydrocarbon structure.

Sunlight is necessary for ozone formation to take place on any appreciable scale, since the reaction is photochemical in nature. Higher temperatures also facilitate the reaction.

Meteorological conditions (cloud cover, wind, mixing height, humidity, etc.) play a role in determining the concentration of the reactants as well as in influencing temperature and sunlight. If NMHC's and NOx are dispersed quickly by strong winds, ozone production will be slight. On the other hand, stagnant weather conditions can exacerbate the ozone formation problem by holding pollutants in an area and producing high concentrations of ozone precursors (NMHC and NOx).

Thus, meteorological conditions influence diurnal (day/night) and seasonal patterns in O_3 concentrations. Generally, photochemical ozone levels peak in the early afternoon on a daily basis and during the summer months over the course of the year.

The types of NMHC's present also affect ozone formation. Hydrocarbons differ in their weight and molecular structure, which affect their reactivity. This is discussed in detail later.

Hydrocarbon Sources

Hydrocarbons are produced by many sources. The largest share (possibly 80% by mass of all emissions in the U.S.), is emitted by vegetation, especially forests. Anthropogenic (man-made) sources include combustion by industry, evaporation from refineries, and, of course, the automobile. However, even though total natural NMHC emissions may be much greater than anthropogenic ones, they are spread out thinly over wide areas, while industrial and automobile emissions tend to be concentrated in urbanized areas, where a large percentage of the population is located.

Even close to densely wooded areas, the concentration of natural HC's is generally very low, both in actual terms and in relation to total NMHC. Rural sites typically show early morning (peak) NMHC levels of 0.05-0.20 parts per million carbon (ppmC) of which most is due to anthropogenic origin. In urban areas, observations are often five to twelve times higher, with anthropogenic sources dominating the hydrocarbon mix.

Hydrocarbon Reactivities

Natural hydrocarbons are very reactive, however, most natural HC's are terpenes, which react with O_3 to form aerosols in areas with little NO_x (i.e., rural areas). Therefore they act as an ozone sink as well as a source. Anthropogenic HC's do not have as great a potential for aerosol formation. These conclusions are supported by smog chamber data.

Rural and Urban Ozone Production

In rural areas the ratio of HC to NO_x can be as high as 200:1. In urban areas with ozone problems this figure is usually about 10:1, close to the optimum ratio for producing ozone. This difference in ratios is due principally to the fact that NO_x sources are low in rural areas. Therefore, in rural sites, there is insufficient NO_x to drive the photochemical reactions necessary for significant ozone production. The small amount of O_3 which is formed reacts quickly with the excess natural hydrocarbons. Actual ozone measurements for rural areas typically average 0.02-0.05 ppm during the photochemical oxidant season.

The production of O_3 in rural areas is further inhibited by the fact that most of the HC's emitted are produced by natural sources. As described earlier, natural HC's, when present in large excess relative to NO_x , react with ozone rapidly, thus preventing accumulation of ozone to problem levels.

Transport of NMHC's Between Rural and Urban Areas

The high NMHC concentrations of urban areas can affect sites downwind, but naturally produced NMHC's do not seem to be transported to urban areas. The high reactivity of natural hydrocarbons results in a short average lifetime. Thus, only a few species of naturally produced HC's last long enough to travel to urban areas.

Downwind from urban areas, however, both HC and ozone levels can be very high. This is because the anthropogenic HC's are not used up as fast in ozone formation, (they have longer lifetimes), and there are higher HC concentrations than in rural areas to start with.

Natural HC Contribution to the O₃ Problem

The properties of biogenic HC's that have been discussed tend to discount their effects on urban areas. Unlike the man-made hydrocarbons, natural HCs tend to form photochemically unreactive products, such as aerosols. Their short lifetimes mean they are unlikely to contribute to the transport problem. Known ambient hydrocarbon measurements in urban areas bear this out. Natural HC's are never found in significant concentrations in these areas. It is possible that they are not found because they have already reacted to form ozone, but in such a case one would also expect to find significant quantities of aerosols, another product of natural hydrocarbon reactions. This has not been found. It is also possible that the measurements of natural HC emissions are erroneously high. These possibilities have not been resolved yet.

Due to the complex nature of the photochemical reactions involved in ozone formation, and the variables that affect them, the effect described here cannot yet be firmly quantified. However, the tendencies are clear and available data suggest that it is highly unlikely that air quality is significantly affected by emission from vegetation.

Recent Controversial Reports

Two recently publicized reports have ignited controversy on the issue of increased ozone due to natural hydrocarbon production. One, a study by P. R. Zimmerman of Washington State University, measured the NMHC's produced in the Tampa/St. Petersburg area by biogenic and anthropogenic sources. Since the ambient concentrations of NMHC are low, the resulting figure of 68% biogenic hydrocarbon emissions is somewhat questionable.

Another study, by J.S. Sandberg et. al. of the San Francisco Bay Air Pollution Control District, seemed to show a relationship between levels of winter rain and summer ozone, suggesting that increased vegetative growth resulted in increased ozone production. Subsequent studies at University of California/ Riverside (Pitts) did not support such correlations; furthermore Sandberg has not shown a cause and effect relationship to exist, and, in fact, evidence exists to the contrary. Levels of ambient biogenic HC measured in the San Francisco area in the past decade are negligible.

Natural Hydrocarbon Sources and the Ozone Standard

In conclusion, it seems that natural hydrocarbons do not contribute enough to the ozone problem in non-attainment areas to make the ozone standard difficult to meet. In urban areas their concentrations are low due to the relative lack of greenery, and due to insignificant transport from rural areas. These low concentrations do not lead to significant ozone production. In fact, smog chamber experiments indicate that even at an optimum terpene/NOx ratio, about 20 ppbC would produce only 1 ppb ozone.¹¹ In rural areas where natural hydrocarbon concentrations can be higher there are generally not ozone problems, and where there are, the evidence shows anthropogenic/transport origin.

CONCLUSION:

For urban areas, relative to ozone produced from man-made sources, ozone produced by natural hydrocarbons and stratospheric ozone is of little significance on average. However, in certain instances, stratospheric ozone can have a significant impact on peak levels of ozone. The development of better means of detecting and separating the effects of anthropogenic and biogenic ozone, can resolve the conflict surrounding them. Even without this development, however, it is clear that in order to meet ozone air quality standards, anthropogenic sources of ozone precursors must be reduced.

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