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PHOTOCHEMICAL (OXIDANT) AIR POLLUTION  
SUMMARY INFORMATION

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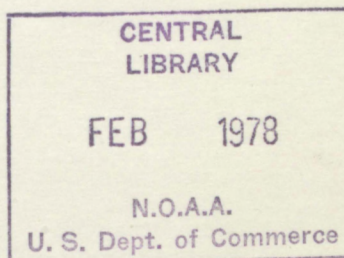
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## 1. INTRODUCTION

This compendium has been written with the National Weather Service's air pollution program in mind. It has been designed to aid in the developing of techniques to forecast meteorological conditions which could produce photochemical problems.

Air pollution resulting from photochemical reactions is a serious problem in many areas across our country. This type of pollution is not confined to urban areas and, in fact, can be just as serious in rural areas.

Since these pollutants result from complex chemical reactions and their character can change with time and space, techniques utilizing only mixing heights, transport winds and ventilation are generally inadequate in predicting the conditions favorable for photochemical oxidant buildups.

This compendium will give an overview of the problem including; (1) chemistry involved, (2) meteorological conditions favorable for the production of the photochemical oxidants, and (3) unique aspects of this type of pollution.



## 2. CHEMISTRY

2.1 INTRODUCTION. Most photochemical pollutants, or oxidants, are secondary pollutants resulting from a series of chemical reactions, triggered by solar radiation and heat, among photochemical oxidant precursors. The precursors are primarily oxides of nitrogen ( $\text{NO}_x$ ) resulting mainly from transportation and stationary power sources, and certain hydrocarbons produced by vehicular exhausts, cleaning fluid evaporation, open burning, and some industrial operations. Literally thousands of different hydrocarbon precursors and great volumes of oxides of nitrogen can be released into the air on a given day. This can result in many different reactions occurring at differing times after precursor release. The oxidant concentrations produced depend upon the types and amounts of the precursors, their emission rates, the intensity of solar radiation plus meteorological factors such as temperature and wind. Oxidant concentrations may be directly measured or trends may be inferred from measurements of the oxidant precursors.

Ozone ( $\text{O}_3$ ) and PAN (peroxyacetyl nitrate) are the two major oxidants produced. Since ozone is such an important pollutant, the following chemistry discussion will concern it.

2.2 OZONE PRODUCTION. The formation and buildup of ozone is initiated by photochemical reactions involving  $\text{NO}_x$  and certain reactive hydrocarbons (HC). An important beginning reaction involves the formation of  $\text{NO}_2$  from NO and a radical species such as  $\text{RO}_2$  (formed from a reactive HC reaction).



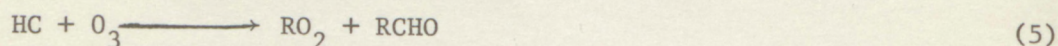
Then,  $\text{NO}_2$  reacts in the presence of sunlight to produce oxygen.



Reaction (2) is relatively fast in strong sunlight and the resulting oxygen atoms (O) combine rapidly with molecular oxygen ( $\text{O}_2$ ) to form ozone ( $\text{O}_3$ ).



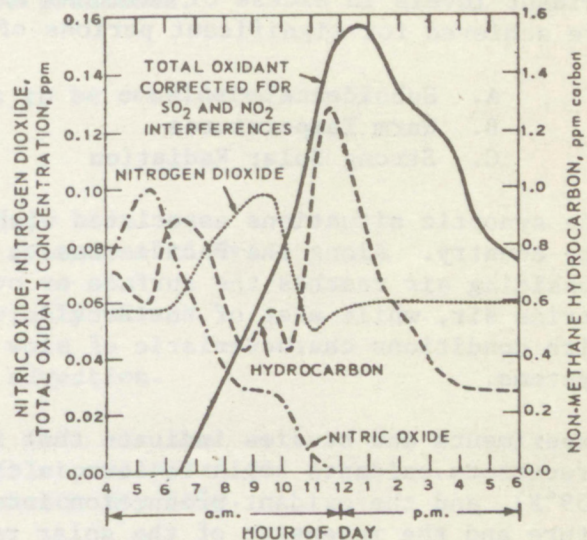
2.3 OZONE DESTRUCTION. After  $\text{O}_3$  is formed, it can be destroyed by other types of reactions.





2.4 DIURNAL VARIATION OF  $O_3$  CONCENTRATIONS. The ozone production and destruction reactions combine to produce a diurnal variation of ozone concentrations (morning minimum and afternoon maximum) which is opposite the cycle common to many other types of air pollution (Figure 1).

Figure 1: Hourly variation of selected pollutants in Philadelphia, July 22, 1967. (From U.S. DHEW Pub Number AP-63, March 1970)



During the morning rush hour, great volumes of oxidant precursors are pumped into the air by automobiles, power plants, industrial parks, etc. The reactions begin and, in the presence of heat and sunlight, the oxidants form. Although some of this ozone is destroyed, the overall concentration increases during the morning and early afternoon as, in addition to the relatively quick reactions involving  $NO_2$  (equation 2), many slower hydrocarbon reactions culminate and begin producing ozone.

By afternoon, the intensity of the incoming solar radiation decreases. If precursor emission continues, the scavenging effect of the  $NO$  (Equation 4) becomes predominate and the ozone concentration begins to decrease. At night, no ozone is being produced and that which is trapped in the night-time mixing layer is greatly reduced by  $NO$  scavenging.

Finally, it should be noted that several California studies have shown that a degradation of visibility often accompanies the photochemical process. The studies have indicated that some of the reactions produce organic particles and these aerosols can reduce the visibility. Also, since many of the aerosols are hygroscopic in nature, they can enhance the occurrence of fog, high humidities, and reduced visibilities.



### 3. METEOROLOGICAL CONDITIONS FAVORABLE FOR PHOTOCHEMICAL OXIDANT PRODUCTION

3.1 OVERVIEW. Nationwide, three conditions generally exist before oxidant levels in excess of National Ambient Air Quality Standards (NAAQS) are achieved for significant periods of time.

- A. Subsidence
- B. Warm Temperatures
- C. Strong Solar Radiation

The synoptic situations associated with the occurrences vary somewhat across the country. Along the Pacific Coast, episodes generally occur when warm, subsiding air reaches the surface or overlays a surface based layer of marine air, while east of the Rockies, episodes are generally associated with conditions characteristic of slow moving, warm core high pressure systems.

Experiments and studies indicate that in the presence of the necessary precursors, oxidants begin to form in the lower atmosphere at around 15°C (59°F), and the oxidant production increases with increases in the temperature and the intensity of the solar radiation. An operationally significant temperature for photochemical pollution problems to begin occurring is around 27°C (80°F). This value will vary across the country and each office should determine the seasonally adjusted significant temperature for its area.

3.2 DEVELOPING REGIONAL GUIDELINES. In developing local meteorological guidelines for identifying favorable conditions for oxidant episodes, the following meteorological parameters should be considered. It should be noted that oxidant problems can exist with the atmosphere ventilating to a degree that would disperse other types of air pollutants. A station's critical mixing height and ventilation values may have to be adjusted to handle oxidant problems. Generally, critical mixing height values will be greater for oxidant considerations.

#### A. Pacific Coast (parameters to be considered)

1. Temperature profile in lowest 2000 meters of atmosphere.  
Investigate the inversion and the structure above and below it.

- 2. Wind speed and direction (below 70 kPa (700mb))
- 3. Surface temperatures
- 4. Solar radiation
- 5. Large scale subsidence as indicated by:

- a. 50 kPa (500 mb) absolute vorticity values



- b. 50kPa heights.
  - c. Negative vorticity advection.
- 6. Inland to coast pressure gradients.
- 7. Seasonal variations
- B. East of Rockies (parameters to be considered)
  - 1. Air mass changes.
  - 2. Maximum temperatures.
  - 3. Wind speed and direction.
  - 4. Large scale subsidence as indicated by:
    - a. 50kPa absolute vorticity values.
    - b. 50kPa heights.
    - c. Negative vorticity advection.
  - 5. Solar radiation.
  - 6. Days since last measurable precipitation
  - 7. Advection - satellite photos may help.

3.3 EXAMPLES OF REGIONAL GUIDELINES. The following are two examples of how two agencies have adjusted the general guidelines given in 3.2 to meet their oxidant forecasting problems. These examples could be used as a starting point for developing other regional guidelines.

3.3.1 PREDICTING OZONE LEVELS WITHIN THE EASTERN LOS ANGELES BASIN - SAN BERNARDINO COUNTY AIR POLLUTION CONTROL DISTRICT.\* An objective scheme utilizing some of the parameters above is used to predict ozone levels for San Bernardino, California. The air pollution meteorologist enters Table I with the values of the observed parameters, then reads the number of points for each from the left hand column. He then sums all the values, includes the monthly and daily correction numbers and obtains a final total. This total corresponds to the expected ozone concentrations in parts per hundred million for that day.

\*Although National Weather Service forecasters don't predict pollution levels, this technique is presented because it shows the strong correlation between certain meteorological parameters and various ozone concentrations.



Points	1 STABILITY	95 KPA TEMP	2 INVERSION	3 GRADIENT	DAY	4 MONTH	PTS.
0	$\leq 5.0$	$\leq 5.0$	1524 +	$\leq -10$ +20		JAN	-15
1	5.1 - 7.0	5.1 - 8.0	1220 - 1524	- 9.0 to - 9.9 +16.0 to +19.9	SUNDAY & HOLIDAY	FEB	-12
2	7.1 - 9.0	8.1 - 11.0	915 - 1219	- 8.0 to - 8.9 +12.0 to +15.9		MAR	-9
3	9.1 - 11.0	11.1 - 14.0	763 - 914	- 7.0 to - 7.9 +10.0 to +11.9	MONDAY TUESDAY WEDNESDAY SATURDAY	APR	-5
4	11.1 - 13.0	14.1 - 17.0	610 - 762 SURFACE	- 6.0 to -6.9 + 8.0 to +9.9	THURSDAY	MAY	0
5	13.1 - 15.0	17.1 - 20.0	458 - 609	- 5.0 to -5.9 + 6.0 to +7.9		JUN	+1
6	15.1 - 17.0	20.1 - 24.0	305 - 457	- 4.0 to -4.9 + 4.0 to +5.9	FRIDAY	JUL	+2
7	17.1 - 19.0	24.1 - 28.0	214 - 304	+ 2.0 to +3.9		AUG	+2
8	19.1 - 21.0	28.1 - 32.0	153 - 213	- 3.0 to -3.9 + 1.0 to +1.9		SEP	+1
9	21.1 - 23.0	32.1 - 36.0	95 - 152	- 2.0 to -2.9 0.0 to +0.9		OCT	-8
						NOV	-11
10	$>23.1$	$>36.1$	46 - 94	- 1.9 to -0.1		DEC.	-15

TABLE I

1. (85kPa temperature - surface temperature) + (temperature of inversion top - temperature of inversion base) = stability degrees Celsius.
2. Height of inversion base in meters.
3. Gradient Summation  $[(P_1 - P_2) + (P_3 - P_4) + (P_5 - P_6)]$   
 where  $P_1$  = Long Beach (LGB) sea level pressure  
 $P_2$  = Daggett (DAG) sea level pressure  
 $P_3$  = San Diego (SAN) sea level pressure  
 $P_4$  = Las Vegas (LAS) sea level pressure  
 $P_5$  = Norton AFB (SBD) sea level pressure  
 $P_6$  = George AFB (VCV) sea level pressure
4. Correction to point total - is a function of solar radiation and climatology.



### Example

For a Tuesday in March

	<u>Observed Value</u>	<u>Points</u>
a. Stability	12	4
b. 95 kPa Temp.	10	2
c. Inversion	500	5
d. Gradient	+11	3
e. Day	Tuesday	3
f. Month	March	-9
		<hr/> 8 TOTAL

The expected concentration for this day would be 8 parts per hundred million in San Bernardino.

3.3.2 PREDICTING THE NEED FOR OZONE ADVISORIES IN ILLINOIS. The Illinois Environmental Protection Agency has developed objective meteorological guidelines to help them forecast the need for ozone advisories. The scheme determines whether an ozone advisory should be issued for tomorrow if an advisory is in effect today.

#### A. Guidelines

1. No significant air mass change is expected for the next 24 hours. No "significant air mass change" is interpreted to be the passage of a cold front or an occluded front such that there is a resulting drop in the temperature and/or specific humidity at a given location. If the front is weak, slow moving (as represented by a stationary front), or ill defined (as the tail end of a cold front), then there is reasonable doubt as to whether or not there will be a significant air mass change for the next day. The passage of a warm front is considered a positive factor in the expected reoccurrence of elevated ozone.

2. Maximum temperature forecast (tomorrow) to equal or exceed 14°C (58°F).

3. Sky condition forecast of 0.8 cloud coverage or less for 1100 local time tomorrow.

4. Tomorrow's surface wind forecast to be less than 25 KMH (15 MPH) or if southerly less than 32 KMH (20 MPH).

In addition to the guidelines used for declaring an ozone advisory, the following criteria are used to determine if a more serious alert is warranted.

1. No significant change in air mass location or intensity, i.e., a decrease of less than 60 meters in the 500 mb height, no passage



of ridge or trough line at 500 mb, movement of surface high pressure center less than 200 miles.

2. No significant decrease in maximum afternoon temperature, i.e., less than 5°F temperature decrease.

3. No significant increase in cloudiness, i.e., no ceiling forecast between 10 a.m. and 4 p.m. of the next day.

4. No significant increase in surface wind speed, i.e., less than 5 knots.

5. No significant change in wind direction, i.e., wind speed magnitude times wind direction change magnitude is equal to a value less than 300. For light and variable winds, a change in transport wind direction of less than 45 degrees.



#### 4. UNIQUE ASPECTS OF PHOTOCHEMICAL AIR POLLUTION

4.1 PEAK CONCENTRATIONS AND TIMES OF OCCURRENCE. Unlike the morning maximum and afternoon minimum concentration value cycle common to most non-reactive pollutants, oxidant concentration levels are generally the lowest near sunrise and reach maximum level in the afternoon or early evening (Figure 1). The time of maximum concentration generally occurs later in rural areas and, in some cases, the values of both maximum and minimum oxidant levels are greater in the rural areas (Figure 3). This discovery was quite unexpected and perplexing. However, the following fact may explain the phenomenon. Ozone is destroyed by contact with NO which comes primarily from automobiles in urban areas. Since there is not as great a concentration of NO in rural areas, less ozone is scavenged.

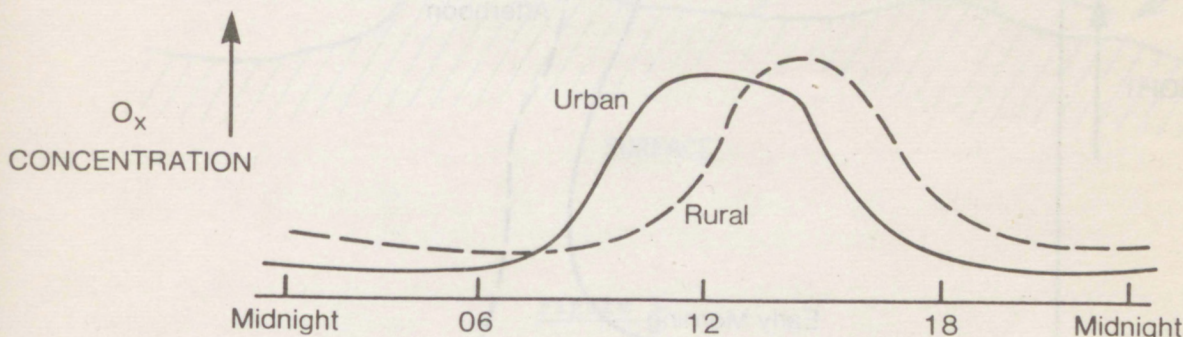


Figure 3  
Urban vs. rural diurnal oxidant concentration variation

4.2 OXIDANT TRANSPORT. In rural areas, peak concentrations occur later because much of the problem results from oxidants produced in urban areas and then advected to the rural areas. Also the less reactive compounds sometimes do not react to form oxidants until they have moved from the urban areas. So, the farther (i.e., downwind) a site is from major oxidant precursor sources, the later the peak concentration. Studies have shown very significant advection of photochemical air pollution. One demonstrated that photochemical pollution resulting from precursor emissions in the New York City metropolitan area could be advected as far as 300 kilometers (186 miles) to the northeast, reaching northeast Massachusetts. On the other hand, researchers in the New York City area believe they can show that a large percent of their pollution is advected from industrial areas far to the west. In Europe, studies have documented ozone transport of up to 1000 kilometers (621 miles).



4.3 OZONE CONCENTRATIONS WITH HEIGHT. A pool of ozone with relatively constant concentrations remains aloft at night. The following morning this pool is tapped after daytime vertical mixing develops and contributes to the increasing ozone levels at ground level. (See Figure 4.)

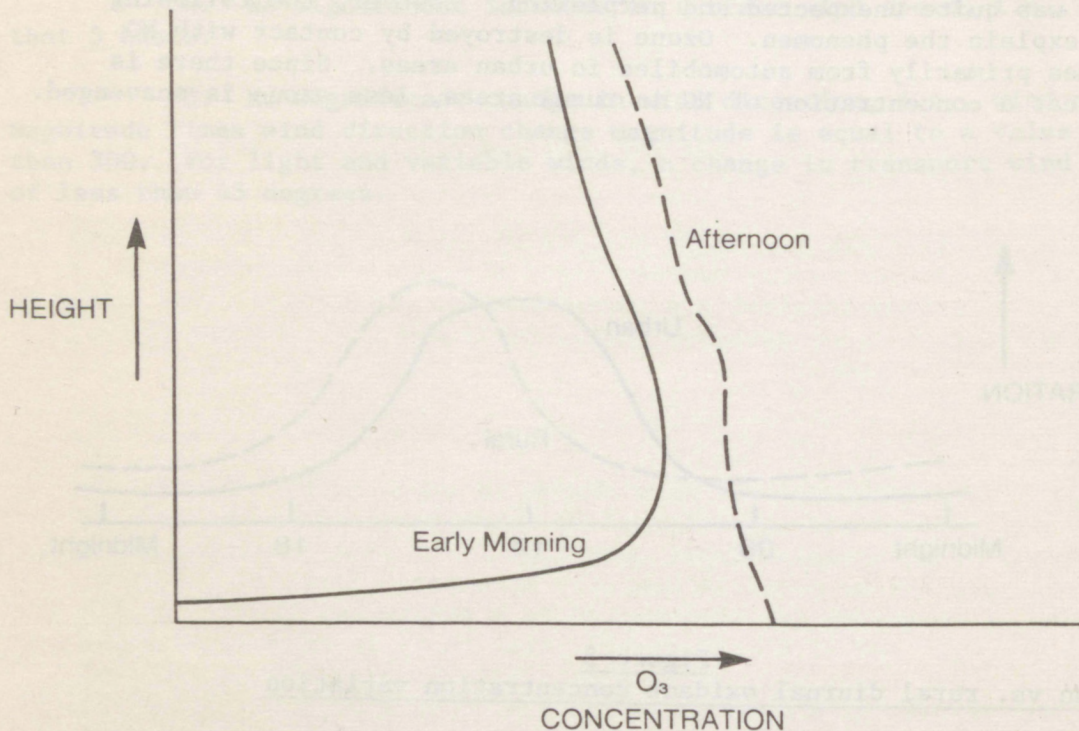


Figure 4  
Morning and Afternoon Ozone Concentrations vs. Height

4.4 UNEXPECTEDLY HIGH OZONE CONCENTRATIONS. At times, total oxidant or ozone values remain high throughout the night or levels soar at unexpected times, such as during the very early morning hours. These episodes can be caused by transport, however, often they are the result of large scale



fumigation. In such cases, low-level instability does not allow the formation of the nighttime inversion or breaks a weak inversion tapping the ozone pool aloft. (See Figure 5.)

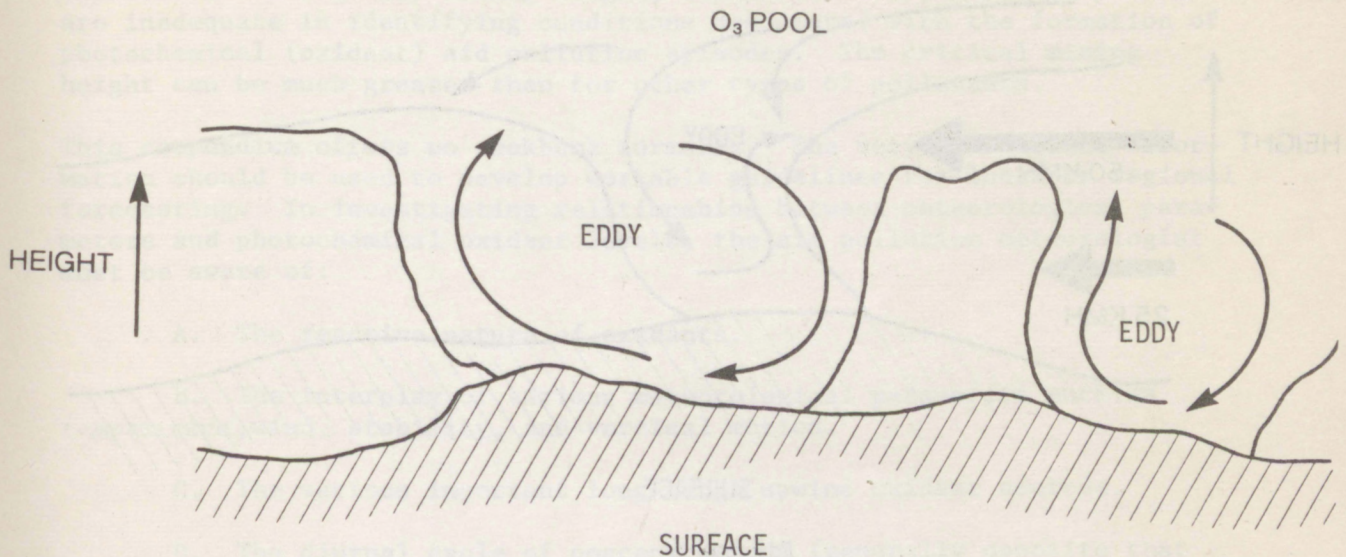


Figure 5

Tapping of an Elevated Ozone Source Produced by  
Low-Level Instability

4.5 HIGH OZONE CONCENTRATIONS WITH STRONG WINDS. Ozone levels may remain high for several hours after a strong, gusty (25 to 40 kmh or about 15 to 20 knots) wind begins to blow. Often, in such cases, the winds are accompanied by low-level wind speed shear and, if sufficient shear develops, eddies can bring elevated sources of ozone to the surface. This phenomena is often noted at the end of a prolonged episode or "stagnation" condition and can exist for several hours until the elevated source is dispersed.



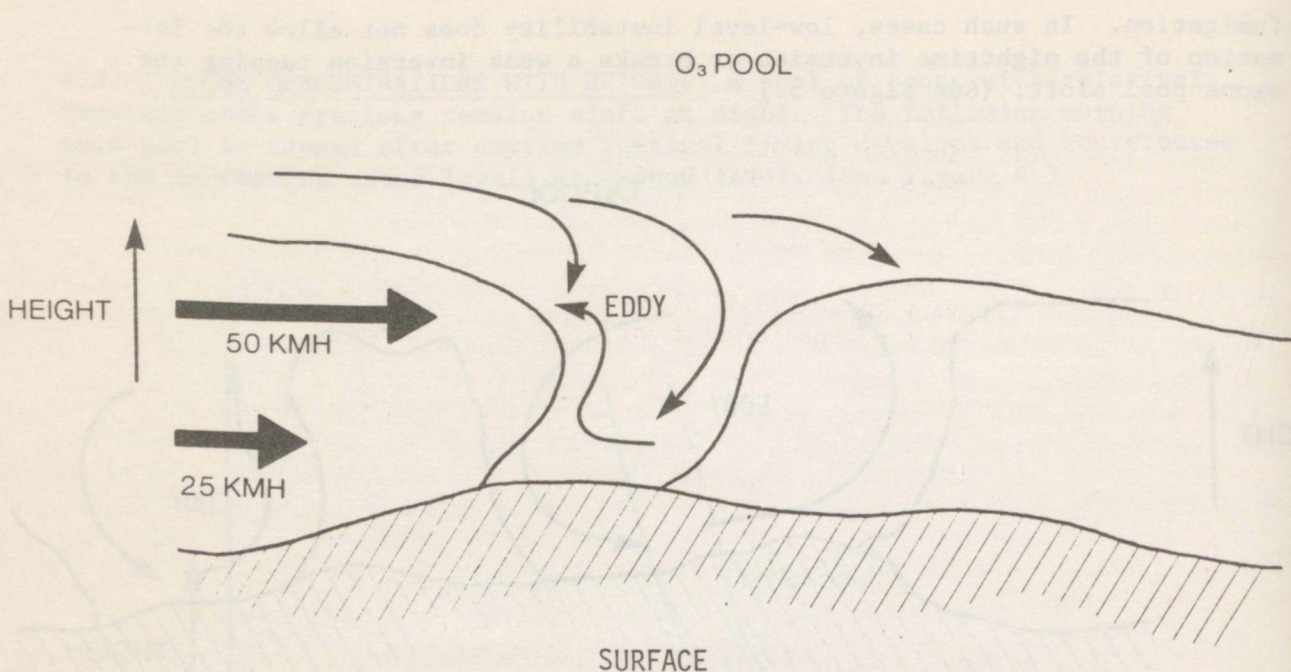


Figure 6

Eddies, Produced by Low Level Wind Speed Shear,  
Tapping an Elevated Ozone Source

4.6 SIGNIFICANT SHORT-LIVED OCCURRENCES. Another oddity is the jump in ozone levels that can occur with thunderstorms, squall lines, frontal passages, and tropical storms. The vigorous downward motion of these systems tap elevated sources of ozone and carry the high ozone concentrations to ground level. Concentrations of ozone from these occurrences can exceed the National Ambient Air Quality Standard (0.08 ppm). Although the episodes usually last only for a few hours, the ozone concentrations can be high enough to damage ozone sensitive plants. These short-lived occurrences may be significant in agricultural areas.



## 5. CONCLUSION

Photochemical air pollution is probably the most meteorologically dependent of all types of air pollution. As such, air pollution meteorological criteria stressing only mixing height, transport winds, and ventilation are inadequate in identifying conditions associated with the formation of photochemical (oxidant) air pollution episodes. The critical mixing height can be much greater than for other types of pollutants.

This compendium offers no cookbook formulas. The very generalized information should be used to develop workable guidelines for local or regional forecasting. In investigating relationships between meteorological parameters and photochemical oxidant levels, the air pollution meteorologist must be aware of:

- A. The reactive nature of oxidants.
- B. The interplay of various meteorological parameters such as temperature, wind, stability, and vertical motion.
- C. The various important long-range upwind oxidant sources.
- D. The diurnal cycle of concentrations (generally opposite that of non-reactive pollutants).



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