

## **CHAPTER 12. OZONE AIR POLLUTION**

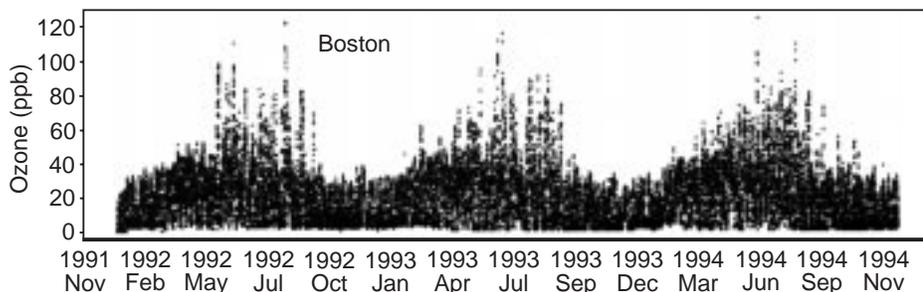
So far we have emphasized the beneficial nature of tropospheric  $O_3$  as the precursor of OH. In surface air, however,  $O_3$  is toxic to humans and vegetation because it oxidizes biological tissue. As we have seen in chapter 11,  $O_3$  is produced in the troposphere from the oxidation of CO and hydrocarbons by OH in the presence of  $NO_x$ . In densely populated regions with high emissions of  $NO_x$  and hydrocarbons, rapid  $O_3$  production can take place and result in a surface air pollution problem. We describe in this chapter the  $O_3$  pollution problem in the United States, examine the factors controlling  $O_3$  concentrations, discuss the efficacy of emission control strategies, and conclude by linking the regional air pollution problem back to the global budget of tropospheric  $O_3$ .

### **12.1 AIR POLLUTION AND OZONE**

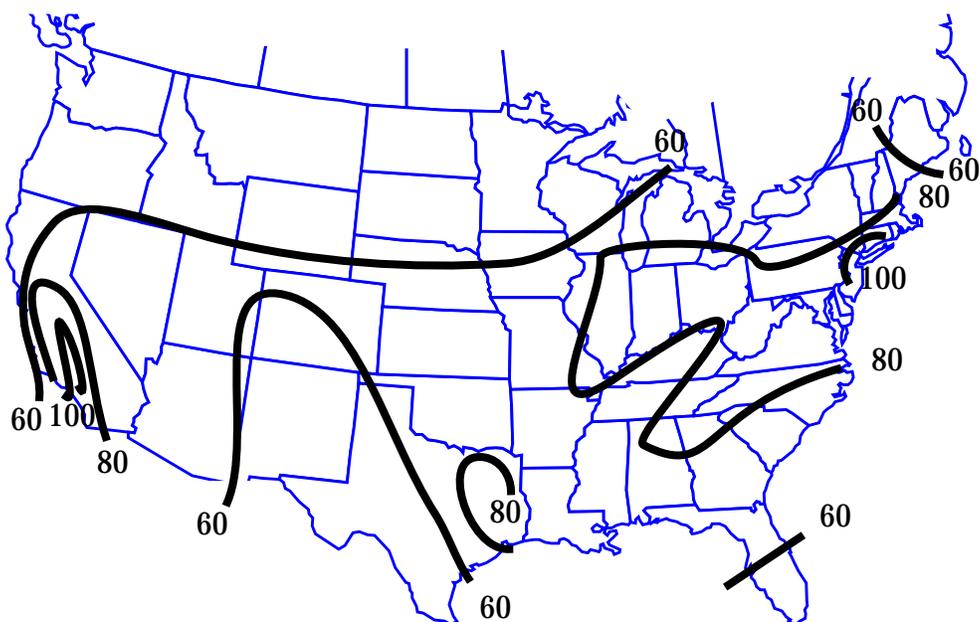
Fuel combustion and other activities of our industrial society release into the atmosphere a large number of pollutants which can, by direct exposure, be harmful to public health or vegetation. This air pollution is generically called “smog” because it is associated with reduced visibility. The low visibility is due to scattering of solar radiation by high concentrations of anthropogenic aerosols (section 8.2.2). The health hazards of smog are caused in part by the aerosol particles but also by invisible toxic gases including  $O_3$ , CO,  $SO_2$ , and carcinogens present in the polluted air together with the aerosols. In the United States and in most other industrialized countries, air quality standards (concentrations not to be exceeded) have been imposed to protect the population against exposure to different air pollutants. When the standards are exceeded, emission controls must be enacted. National legislation for air pollution control in the United States started with the Clean Air Act of 1970. Since then,  $O_3$  has proven to be the most difficult pollutant to bring into compliance with air quality standards.

Concentrations of  $O_3$  in clean surface air are in the range 5-30 ppbv. The air quality standard for  $O_3$  in the United States, newly revised as of 1997, is a maximum 8-hour average  $O_3$  concentration of 84 ppbv not to be exceeded more than three times per year. Figure 12-1 shows a three-year time series of  $O_3$  concentrations measured at Boston, Massachusetts. Concentrations peak in summer when production is most active (chapter 11) and

occasionally exceed 84 ppbv. There is a large day-to-day variability reflecting meteorological conditions. Concentrations of  $O_3$  are highest under stagnant conditions associated with strong subsidence inversions which allow pollutants to accumulate near the surface (section 4.3.5).



**Figure 12-1** Time series of  $O_3$  concentrations measured in Boston, Massachusetts.



**Figure 12-2** 90th percentiles of summer afternoon ozone concentrations measured in surface air over the United States. "90th percentile" means that concentrations are higher 10% of the time. Adapted from Fiore, A.M., et al., *J. Geophys. Res.*, 103, 1471-1480, 1998.

Figure 12-2 shows the 90th percentile concentrations of summer afternoon  $O_3$  concentrations in surface air over the United States. Values in excess of 80 ppbv are found over large areas of the country. Concentrations are highest over southern California, eastern Texas, the industrial midwest, and the mid-Atlantic eastern states, reflecting roughly the distribution of population. Within a given region, there is little difference in  $O_3$  concentrations between

cities, suburbs, and nearby rural areas;  $O_3$  is a regional rather than urban pollution problem. In Massachusetts, for example,  $O_3$  concentrations tend to be highest not in Boston but in rural western Massachusetts and Cape Cod which are frequently downwind of metropolitan areas to the southwest. The broad spatial extent of the  $O_3$  pollution problem has important implications not only for population exposure but also for effects on crops and forests. There is abundant evidence that sensitive crops are damaged by  $O_3$  concentrations as low as 40 ppbv, well below the current air quality standard.

The presence of high concentrations of  $O_3$  in smog was first discovered in Los Angeles in the 1950s. Laboratory chamber experiments conducted at the time showed that  $O_3$  was generated by photochemical reactions in the atmosphere involving hydrocarbons and  $NO_x$  emitted from automobiles. This atmospheric mechanism for  $O_3$  production helped to explain why  $O_3$  concentrations are often higher downwind of urban areas than in the urban areas themselves. The details of the chemical mechanism were poorly understood until the 1970s, however, because the essential role of OH as a hydrocarbon oxidant was not recognized (section 11.1). Before then it was thought that hydrocarbons would be oxidized by O atoms originating from the photolysis of  $O_3$  and  $NO_2$ . We now know that hydrocarbon oxidation by O atoms is negligibly slow and that OH is the critical hydrocarbon oxidant driving  $O_3$  formation. In the next section we examine in more detail the chemistry of  $O_3$  pollution and discuss the implications for control strategies.

## 12.2 OZONE FORMATION AND CONTROL STRATEGIES

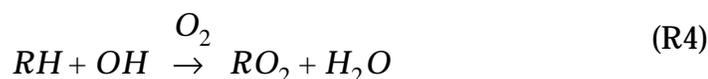
The high concentrations of  $O_3$  in surface air over the United States arise from high emissions of  $NO_x$  and of various reactive hydrocarbons (including alkanes, alkenes, aromatics, and multifunctional compounds). The emission of  $NO_x$  is mainly from fossil fuel combustion (section 11.4). The hydrocarbons are emitted by a range of human activities including combustion, fuel evaporation, solvent use, and chemical manufacturing. They also have a large natural source from terrestrial vegetation (the smell of a pine forest, for example, is due to natural hydrocarbons).

Production of  $O_3$  in polluted air follows the same chain reaction mechanism as described in Chapter 11. The chain is initiated by

production of HO<sub>x</sub>,



and is propagated by reaction of OH with hydrocarbons. We use *RH* (where *R* is an organic group) as simplified notation for hydrocarbons. Oxidation of a hydrocarbon by OH produces an organic peroxy radical RO<sub>2</sub>:

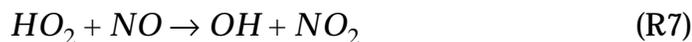


The relative importance of different hydrocarbons in driving reaction (*R4*) can be measured in terms of their abundance and their reactivity with OH. The reactivity generally increases with the size of the hydrocarbon because of the larger number of C-H bonds available for H abstraction by OH; unsaturated hydrocarbons are also highly reactive because OH adds rapidly to the C=C double bonds. In surface air over the United States, large alkanes and unsaturated hydrocarbons are sufficiently abundant to dominate over CO or CH<sub>4</sub> as sinks of OH, in contrast to the remote troposphere (chapter 11).

The RO<sub>2</sub> radical produced in (*R4*) reacts with NO to produce NO<sub>2</sub> and an organic oxy radical RO:



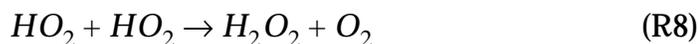
NO<sub>2</sub> goes on to photolyze and produce O<sub>3</sub>. The RO radical has several possible fates. It may react with O<sub>2</sub>, thermally decompose, or isomerize. The subsequent chemistry is complicated. Typically, carbonyl compounds and a HO<sub>2</sub> radical are produced. A generic representation of the reaction, following the fate of CH<sub>3</sub>O described in section 11.3.3, is



The carbonyl compound  $R'CHO$  may either photolyze to produce  $HO_x$  (branching the chain, as we saw for  $CH_2O$  in section 11.3.3) or react with  $OH$  to continue the chain propagation. The net reaction (R4)-(R7) is



The chain is terminated by loss of  $HO_x$  radicals. This loss takes place in two principal ways. When  $NO_x$  concentrations are not too high, peroxy radicals may react with themselves instead of with  $NO$  to produce peroxides and other oxygenated compounds. The most important process is the self-reaction of  $HO_2$ , as in the remote troposphere (section 11.3.2):



At very high  $NO_x$  concentrations, the dominant sink for  $HO_x$  radicals is the oxidation of  $NO_2$  by  $OH$ :

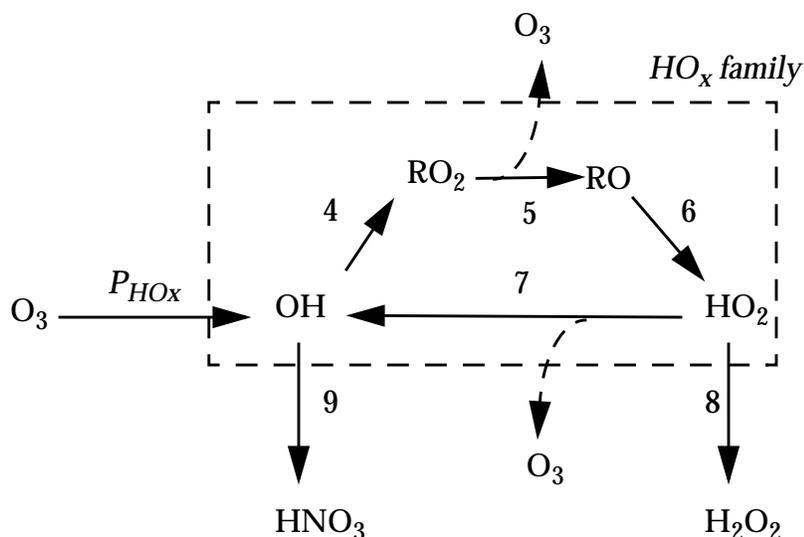
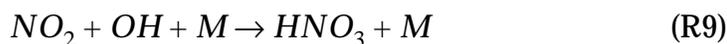


Figure 12-3 Cycling of  $HO_x$  and  $O_3$  production in a polluted atmosphere.

Figure 12-3 is a diagram of the mechanism. The organic radicals  $RO_2$  and  $RO$  propagate the reaction chain and are thus considered part of the  $HO_x$  radical family. One chain propagation cycle (R4)-(R7) produces two  $O_3$  molecules (one from reaction (R5) and one from reaction (R7)). In a polluted atmosphere, we can assume

that chain propagation is efficient so that  $\text{rate}(R4) = \text{rate}(R5) = \text{rate}(R6) = \text{rate}(R7)$ . The rate of  $O_3$  production,

$$P_{O_3} = k_5[RO_2][NO] + k_7[HO_2][NO] \quad (12.1)$$

can be written equivalently

$$P_{O_3} = 2k_7[HO_2][NO] \quad (12.2)$$

The efficient cycling also implies a steady state for OH defined by a balance between production from (R7) and loss from (R4):

$$[OH] = \frac{k_7[HO_2][NO]}{k_4[RH]} \quad (12.3)$$

Consider now the steady-state equation for the  $HO_x$  radical family,

$$P_{HO_x} = k_8[HO_2]^2 + k_9[NO_2][OH][M] \quad (12.4)$$

In the limiting case of low  $NO_x$  concentrations,  $\text{rate}(R8) \gg \text{rate}(R9)$  and the second term on the right-hand side of equation (12.4) can be neglected. Substituting (12.3) into (12.2) yields:

$$P_{O_3} = 2k_7 \left( \frac{P_{HO_x}}{k_8} \right)^{\frac{1}{2}} [NO] \quad (12.5)$$

Note that  $O_3$  production varies linearly with the NO concentration but is independent of hydrocarbons (except for the effect of branching reactions on  $P_{HO_x}$ ). This case is called the  *$NO_x$ -limited regime* because the  $O_3$  production rate is limited by the supply of  $NO_x$ .

Consider now the other limiting case where  $NO_x$  concentrations are high so that  $\text{rate}(R8) \ll \text{rate}(R9)$ . In that case the first term on the right-hand side of equation (12.4) can be neglected, and rearrangement of (12.4) yields:

$$[OH] = \frac{P_{HO_x}}{k_9[NO_2][M]} \quad (12.6)$$

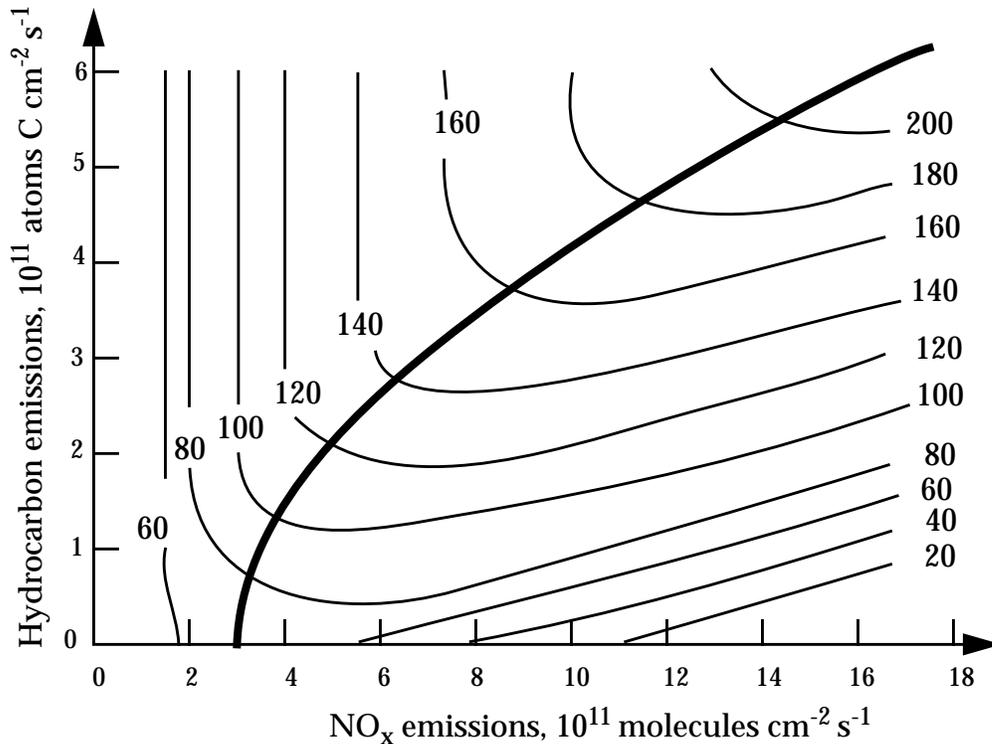
which can then be replaced into (12.3) to give:

$$[HO_2] = \frac{P_{HO_x} k_4 [RH]}{k_7 k_9 [NO][NO_2][M]} \quad (12.7)$$

Further replacement into (12.2) gives:

$$P_{O_3} = \frac{2k_4 P_{HO_x} [RH]}{k_9 [NO_2][M]} \quad (12.8)$$

which indicates that  $O_3$  production increases linearly with hydrocarbon concentrations but varies inversely with  $NO_x$  concentrations. This case is called the *hydrocarbon-limited regime* because the  $O_3$  production rate is limited by the supply of hydrocarbons. The dependence of  $O_3$  production on  $NO_x$  and hydrocarbons is very different between the two regimes.



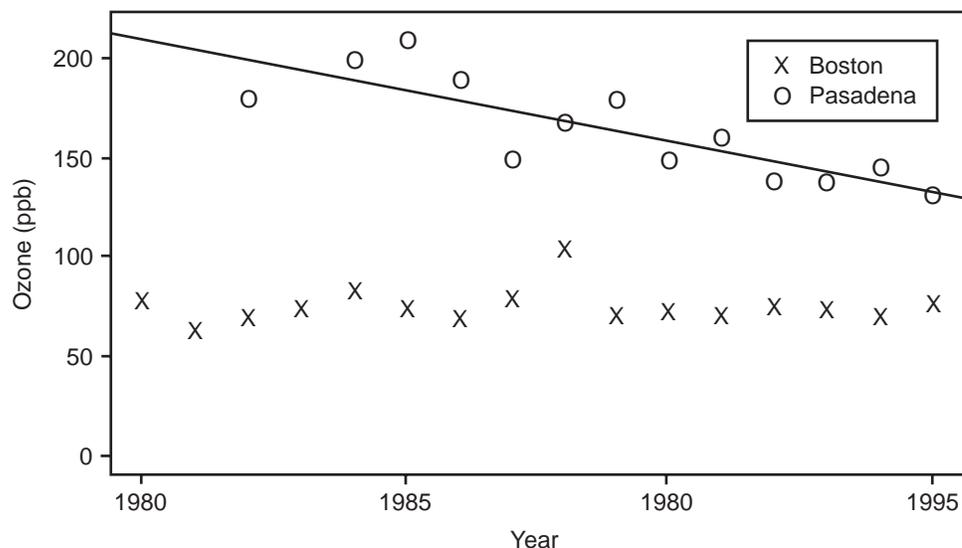
**Figure 12-4** Ozone concentrations (ppbv) simulated by a regional photochemical model as a function of  $NO_x$  and hydrocarbon emissions. The thick line separates the  $NO_x$ -limited (top left) and hydrocarbon-limited (bottom right) regimes. Adapted from Sillman, S., et al., *J. Geophys. Res.*, 95, 1837-1852, 1990.

Figure 12-4 shows the results of a chemical model calculation where  $O_3$  concentrations simulated over the eastern United States are plotted as a function of  $NO_x$  and hydrocarbon emissions. The thick line on the Figure separates the  $NO_x$ - and hydrocarbon-limited regimes. To the left of the line is the  $NO_x$ -limited regime:  $O_3$  concentrations increase with increasing  $NO_x$  and are insensitive to hydrocarbons. To the right of the line is the hydrocarbon-limited regime:  $O_3$  concentrations increase with increasing hydrocarbons and decrease with increasing  $NO_x$ . The non-linear dependence of  $O_3$  on precursor emissions is readily apparent. In the  $NO_x$ -limited regime, hydrocarbon emission controls are of no benefit for decreasing  $O_3$ . In the hydrocarbon-limited regime,  $NO_x$  emission controls cause an *increase* in  $O_3$ .

Formulation of a successful strategy against  $O_3$  pollution evidently requires a knowledge of the chemical regime for  $O_3$  production. Successive generations of atmospheric chemistry models have been developed to address this issue. The first models developed after the 1970 Clean Air Act concluded that  $O_3$  production was in general hydrocarbon-limited. This finding led to a strong regulatory effort to control hydrocarbon emissions from automobiles and industry. Emissions of  $NO_x$  were also controlled, due at least initially to concern over the health effects of  $NO_2$  (a hazardous pollutant in its own right), but the effort was less than for hydrocarbon emissions. Controlling emissions has been an uphill battle because of the continuously rising population and fuel combustion per capita. Between 1980 and 1995, anthropogenic emissions of hydrocarbons in the United States decreased by 12% and  $NO_x$  emissions remained constant, a significant achievement considering that population grew by 20% and automobile usage rose by 60%. Some areas such as Los Angeles enacted even more stringent emission reduction policies than the rest of the nation.

Have these control strategies been successful? Analyses of long-term trends in  $O_3$  concentrations over the United States for the past two decades indicate significant decreases in the Los Angeles Basin and in the New York City metropolitan area, but no significant amelioration over the rest of the country. To illustrate this point we show in Figure 12-5 the trends of 90th percentile concentrations for 1980-1995 in Pasadena (Los Angeles Basin) and Boston. Although the worst offenders of the air quality standard have shown improvement, no improvement is apparent in large

areas of the country where the standard is violated. This mixed success has caused air pollution control agencies to rethink their emission control strategies.



**Figure 12-5 Long-term trends in the 90th percentile summer afternoon concentrations of O<sub>3</sub> in Pasadena (Los Angeles Basin) and Boston for the period 1980-1995. There is a significant decreasing trend in Pasadena (the regression line is shown) but no significant trend in Boston. The high 1988 concentrations in Boston were due to anomalously stagnant weather over the eastern United States that summer. From Fiore et al., op. cit.**

An important discovery in the past decade is that the focus on hydrocarbon emission controls to combat O<sub>3</sub> pollution may have been partly misdirected. Measurements and model calculations now show that O<sub>3</sub> production over most of the United States is primarily NO<sub>x</sub>-limited, not hydrocarbon-limited. The early models were in error in part because they underestimated emissions of hydrocarbons from automobiles, and in part because they did not account for natural emission of biogenic hydrocarbons from trees and crops. As can be seen from Figure 12-4, an upward revision of hydrocarbon emissions (upward translation along the hydrocarbon coordinate) can shift the chemical regime from hydrocarbon- to NO<sub>x</sub>-limited.

The principal biogenic hydrocarbon contributing to O<sub>3</sub> formation is isoprene, CH<sub>2</sub>=CH-C(CH<sub>3</sub>)=CH<sub>2</sub>, an odorless compound which is a by-product of photosynthesis. Isoprene is a diene (two double bonds) and therefore reacts extremely rapidly with OH; its atmospheric lifetime is less than one hour and its decomposition can produce large amounts of O<sub>3</sub> and HO<sub>x</sub>. Emission of isoprene

by vegetation was discovered only in the 1960s, and reliable emission inventories were not available until the 1990s. These inventories now show that isoprene emission in the United States is larger than the sum of all anthropogenic hydrocarbon emissions; even without anthropogenic hydrocarbons, isoprene emission would be sufficient to make  $O_3$  production  $NO_x$ -limited everywhere in the United States except in large urban centers. It appears on the basis of present knowledge that future improvements in  $O_3$  air quality over the United States will require a vigorous program of  $NO_x$  emission controls.

### 12.3 OZONE PRODUCTION EFFICIENCY

We saw in the previous section that  $O_3$  production in the  $NO_x$ -limited regime depends linearly on the  $NO_x$  concentration (equation (12.5)). One might hope under these conditions that a reduction in  $NO_x$  emissions would lead to a proportional decrease of  $O_3$  production. This is however not the case. An important concept introduced in the late 1980s is the  $O_3$  production efficiency  $\epsilon$ , defined as the number of  $O_3$  molecules produced per molecule of  $NO_x$  consumed:

$$\epsilon = \frac{P_{O_3}}{L_{NO_x}} \quad (12.9)$$

where  $L_{NO_x}$  is the loss rate of  $NO_x$ . Here  $\epsilon$  is the chain length when  $NO_x$  is viewed as the propagating agent in the chain mechanism for  $O_3$  production. A  $NO_x$  molecule emitted to the atmosphere undergoes a number  $\epsilon$  of peroxy + NO reactions, producing  $O_3$ , before being converted to  $HNO_3$  which is removed mainly by deposition (Figure 12-6).

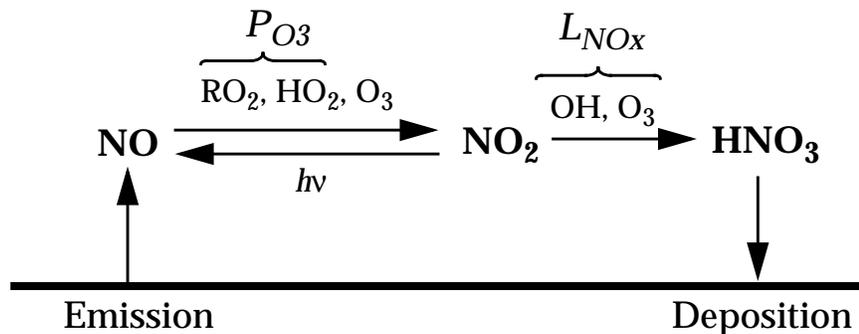


Figure 12-6 Ozone production efficiency  $\epsilon = P_{O_3}/L_{NO_x}$

The perspective of viewing  $\text{NO}_x$  as the propagating agent for  $\text{O}_3$  production is different from the perspective taken in section 12.2 where  $\text{HO}_x$  was viewed as the propagating agent. Both perspectives are equally valid and yield different kinds of information, as we will now see.

Assuming steady state for  $\text{NO}_x$  as represented by Figure 12-6, the  $\text{O}_3$  production efficiency relates the amount of  $\text{NO}_x$  emitted to the corresponding amount of  $\text{O}_3$  produced. A simple analytical expression for  $\varepsilon$  can be obtained for the limiting case where oxidation of  $\text{NO}_2$  by OH (*R9*) is the only sink of  $\text{NO}_x$ :

$$\varepsilon = \frac{2k_7[\text{HO}_2][\text{NO}]}{k_9[\text{NO}_2][\text{OH}]} \quad (12.10)$$

Assuming efficient  $\text{HO}_x$  cycling (Figure 12-3), we can replace the  $[\text{HO}_2]/[\text{OH}]$  ratio using equation (12.3):

$$\varepsilon = \frac{2k_4[\text{RH}]}{k_9[\text{NO}_2]} \quad (12.11)$$

We see that the  $\text{O}_3$  production efficiency increases with increasing hydrocarbon concentrations and decreases with increasing  $\text{NO}_x$  concentration. Increasing hydrocarbon concentrations causes OH to decrease due to (*R4*), therefore increasing the lifetime of  $\text{NO}_x$  and allowing more  $\text{O}_3$  production per molecule of  $\text{NO}_x$  emitted. Increasing  $\text{NO}_x$  conversely causes OH to increase by (*R7*). Values of  $\varepsilon$  over the United States are typically in the range 1-20 mol/mol.

The inverse dependence of  $\varepsilon$  on  $[\text{NO}_x]$  in equation (12.11) suggests somewhat incongruously that the total amount of  $\text{O}_3$  produced from a  $\text{NO}_x$  emission source should be independent of the  $\text{NO}_x$  emission rate, since a decrease of  $\text{NO}_x$  concentration results in a compensating increase of  $\varepsilon$ . Decreasing the  $\text{NO}_x$  emission rate would slow down  $\text{O}_3$  production, but the total amount of  $\text{O}_3$  eventually produced would remain the same. In fact, the dependence of  $\varepsilon$  on  $[\text{NO}_x]$  is not as strong as indicated by equation (12.11) due to the presence of other sinks for  $\text{NO}_x$  aside from reaction with OH (section 11.4). Also, the assumption of efficient  $\text{HO}_x$  cycling behind equation (12.3) applies only to high  $\text{NO}_x$  concentrations (since  $\text{HO}_x$  cycling is driven by NO). Nevertheless,

the negative dependence of  $\epsilon$  on  $[NO_x]$  dampens the  $O_3$  decrease to be expected from a given reduction of  $NO_x$  emissions. Detailed models for the United States predict that a 50% reduction of  $NO_x$  emissions from fossil fuel combustion would decrease summertime  $O_3$  concentrations by only about 15%. Achieving compliance with air quality standards may require draconian controls on  $NO_x$  emissions.

Another important application of the concept of  $O_3$  production efficiency is to understand how changes in  $NO_x$  emissions from fossil fuel combustion might affect global tropospheric  $O_3$ . Fossil fuel combustion accounts presently for 50% of global  $NO_x$  emissions (section 11.4), and one might be concerned that reduction of these emissions to fight  $O_3$  pollution could have negative consequences for the oxidizing power of the atmosphere. However, most of the  $NO_x$  emitted by fossil fuel combustion is oxidized within the region of emission, where  $NO_x$  concentrations are high and  $\epsilon$  is much less than in the remote troposphere. This  $NO_x$  makes therefore relatively little contribution to global tropospheric  $O_3$ . Global models of tropospheric chemistry indicate that fossil fuel combustion in the United States contributes only about 5% to the global source of tropospheric  $O_3$  even though it contributes 15% of the source of  $NO_x$ .

*Further reading:*

**National Research Council**, *Rethinking the ozone problem in urban and regional air pollution*, National Academy Press, Washington, DC, 1991. Review of current knowledge and outstanding issues in ozone pollution.