PROBLEMS

12. 1 NO_x- and hydrocarbon-limited regimes for ozone production

We model the lower troposphere over the eastern United States as a well-mixed box of height 2 km extending 1000 km in the east-west direction. The box is ventilated by a constant wind from the west with a speed of 2 m s^{-1}. The mean NO_x emission flux in the eastern United States is $2x10^{11}$ molecules cm^{-2} s^{-1}, constant throughout the year. Let P_{HOx} represent the production rate of HO_x in the region. As seen in this chapter, we can diagnose whether O_3 production in the region is NO_x- or hydrocarbon-limited by determining which one of the two sinks for HO_x, (1) or (2), is dominant:

$$HO_2 + HO_2 \rightarrow H_2O_2 + O_2 \qquad (1)$$

$$NO_2 + OH + M \rightarrow HNO_3 + M \qquad (2)$$

We present here a simple approach for making this diagnosis.

1. The NO_x emitted in the eastern United States has a lifetime of 12 hours against oxidation to HNO_3 by reaction (2). Assume reaction (2) to be the only sink for NO_x (a fair approximation during summer). Calculate the fraction of emitted NO_x that is oxidized within the region (vs. ventilated out of the region). You should find that most of the NO_x emitted in the eastern United States is oxidized within the region.

2. A photochemical model calculation indicates a 24-hour average HO_x production rate P_{HOx} = $4x10^6$ molecules cm^{-3} s^{-1} over the eastern United States in July. Compare this source of HO_x to the source of NO_x. Conclude as to whether O_3 production over the eastern United States in July is NO_x- or hydrocarbon-limited.

3. The same photochemical model calculation indicates a 24-hour average HO_x production rate P_{HOx} = $1.0x10^6$ molecules cm^{-3} s^{-1} in October.

3.1. Why is the HO_x production rate lower in October than in July?

3.2 Conclude as to whether ozone production over the eastern United States in October is NO_x- or hydrocarbon-limited.

4. As temperatures decrease in the fall, NO_x may be increasingly removed by

$$RO_2 + NO_2 + M \rightarrow RO_2NO_2 + M \qquad (3)$$

where RO_2NO_2 is an organic nitrate such as PAN (in summer, the organic nitrates decompose back to NO_x because of the high temperatures). Consider a situation where reaction (3) represents the main HO_x sink.

4.1 Write an equation for the O_3 production rate as a function of P_{HOx}, [NO], and $[NO_2]$.

4.2 Assuming that the $[NO]/[NO_2]$ ratio is a constant, show that O_3 production is neither NO_x- nor hydrocarbon-limited.

[To know more: Jacob, D.J., et al., Seasonal transition from NO_x- to hydrocarbon-limited O_3 production over the eastern United States in September, *J. Geophys. Res.*, *100*, 9315-9324, 1995.]

12. 2 Ozone titration in a fresh plume

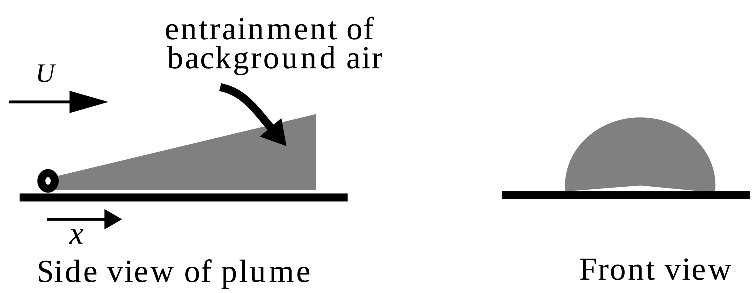
We generally think of NO_x as a source of ozone in urban air. However, ozone can be titrated in a fresh NO_x plume, causing some difficulty in interpreting urban ozone data. Consider a point source at the surface releasing NO continuously at a rate Q (moles s^{-1}). The pollution plume is transported by the mean wind with a constant wind speed U (m s^{-1}). As the plume dilutes it entrains background air containing negligible NO_x and an ozone concentration $[O_3]_b$. We assume that the crosswind extent of the plume at a distance x (m) downwind of the source is a half-disk with radius $R = \alpha x$, where α is a fixed coefficient. We further assume that the plume is well-mixed across its cross-sectional area, and that the only reactions taking place in the plume are

$$NO + O_3 \rightarrow NO_2 + O_2 \qquad (4)$$

$$NO_2 + h\nu \xrightarrow{O_2} NO + O_3 \qquad (5)$$

These two reactions are sufficiently fast that they can be assumed at equilibrium:

$$K = \frac{[NO][O_3]}{[NO_2]}$$



1. Show that the NO_x concentration in the plume at a distance x downwind from the source is given by:

$$[NO_x](x) = \frac{2Q}{\alpha^2 x^2 \pi \beta U}$$

where $[NO_x](x)$ is in units of ppbv, and $\beta = 40 \times 10^{-9}$ is a conversion factor from moles m^{-3} to ppbv; we will use 1 ppbv = 40×10^{-9} moles m^{-3} in what follows.

2. Show that:

$$[O_3](x) = [O_3]_b - [NO_2](x)$$

3. You now have three equations relating [NO](x), $[NO_2](x)$, and $[O_3](x)$. Solve for $[O_3](x)$. Plot $[O_3](x)$ for the following typical values: Q = 5 moles s^{-1}, U = 5 m s^{-1}, K = 10 ppbv, $\alpha = 0.05$, and $[O_3]_b$ = 50 ppbv. How far downwind of the source will the ozone concentration have recovered to 90% of its background value?

[Epilogue: once ozone in the plume has recovered to background levels, further O_3 production takes place in the plume by peroxy+NO reactions followed by reaction (2). Thus the emission of NO_x represents a sink for ozone near the point of emission and a source further downwind.]