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Photochemical Ozone Formation, Simplified

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The intent of this communication is to provide a diagrammatic picture of photochemical ozone formation which nevertheless contains, and in part explains, why reduction of precursor hydrocarbon (HC) emissions makes everyone's ozone exposure lower while reduction in nitric oxide (NO) emissions, the other major precursor, leaves many areas with higher (not lower) ozone exposure.

Fig. 1 is a schematic diagram of ozone formation that nevertheless includes many of the otherwise obscure features of a sophisticated photochemical model. There are four recognizably distinct segments in Fig. 1, lettered A–D and separated by dotted lines. For the most part this understanding comes from Graham Johnson.[1] The base case is represented by the heavy black line. The *x*-axis is labelled as 'time'. If the wind speed is constant, then the *x*-axis could be labelled 'distance'.

The time-dependent processes, which generate photochemical smog, are driven by sunlight and the rates are increased at high temperatures. Typical photochemical smog episodes in Los Angeles or Sydney correspond to segments (B) of 2–4 hours duration and (C) of 8–12 hours duration. If the sunlight ceases before segment (C) terminates, an increasingly frequent observation in the USA, then further ozone formation terminates and the ozone produced slowly dilutes.

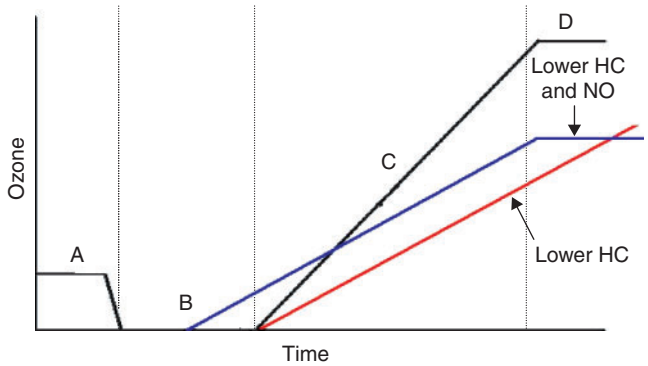

Fig. 1. Schematic cross-section of ozone formation. Wind is assumed to blow at a fixed rate from (A) to (D); time and distance are equivalent. The sections are (A) upwind, (B) central urban area, (C) downwind, (D) further downwind, not often reached because of sunset.

Each segment is dominated by different chemistry, thus:

(A) *Upwind*: There is always ozone encroaching from upwind ozone sources, and even some descending from the stratosphere. In some areas, the ozone arriving in the morning may include significant return flow from the previous day, particularly if the urban area is on a coastline with a typical sea breeze/land breeze diurnal flow pattern. It matters how much ozone comes in from upwind. The more the upwind ozone, the shorter is the titration segment (B)—that is, the segment where urban emissions of NO remove ozone coming in from upwind.

(B) *Titration Segment*: This is the segment in which excess emitted NO from the urban area suppresses ozone by producing NO_2 ($NO + O_3 \rightarrow NO_2 + O_2$). Almost all combustion source NO_x ($NO + NO_2$) is emitted as NO.[2] The more NO is emitted, the longer the ozone concentration level is suppressed. We expect to see ozone levels increasing sooner in time and closer to the urban area during weekends than during weekdays, because NO emissions are lower on weekends; this effect is exactly what is observed. These observations and their implications were reviewed by several authors in the July 2003 issue of the US Air and Waste Management Association's journal *EM*.[3]

The simplest approximation, and the one used in the diagram, places the length of time in (B) as dependent only upon the NO emissions. This is not quite true; solar intensity is necessary and temperature is important. Also as noted above, more ozone coming in from upwind shortens this time. More HC shortens the time somewhat and, most relevant to control measures, less HC lengthens it. All computer models and on-road data (see for instance ref. [4]) suggest that with modern, new vehicle emissions standards, mobile source HC emissions will continue to decline worldwide. This HC reduction alone will increasingly lengthen the titration segment (B).

(C) *HC-Limited*: This is the segment when the complex photochemistry is most apparent and ozone builds up. Johnson's breakthrough in understanding is that the rate of buildup (the angle at which the line in Fig. 1 goes up) is dependent only upon HC (the product of the amount and reactivity) and independent of NO_x. The rate of buildup is also dependent upon the intensity of sunlight and is greater

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at higher temperatures. All the regions under the black sloping (unlabelled) line are HC-limited.

The simplest control measure, the 'HC reduction alone' scenario, is illustrated by the red line ('lower HC'). The ozone buildup occurs more slowly than the base case and the region experiences lower ozone exposure. As HC emissions have gone down nationwide in the United States, the rate of ozone buildup has decreased nationwide. As a result, even places like Los Angeles rarely, if ever, reach segment (D), the NO_x-limited regime, in which ozone ceases to increase with photolysis time. The hydrocarbon-limited region is lasting longer in time and larger in space as HC emissions are reduced.

(D) *NO_x-Limited*: Johnson's other breakthrough observation is that if the sun is present for long enough and the hydrocarbon is reactive enough, the system arrives at segment (D) which has a constant ozone concentration proportional only to the amount of NO_x input. The important understanding of recent trends is that hydrocarbon concentrations and reactivity have gone down so much that even Riverside (well downwind of Los Angeles) hardly ever reaches this NO_x-limited ozone segment before the sun sets (which also stops ozone buildup, even though the amount obtained remains in the HC-limited regime). The continued trend to lower mobile source HC emissions means that there are fewer places that benefit from NO_x reduction. Most people live where ozone levels *increase* if NO_x is reduced. NO_x does contribute to pollution all on its own—Peroxyacetylnitrate (PAN) is a NO_x-derived pollutant molecule of no known benefit, and NO_x, oxidized to nitric acid, acidifies rain, fertilizes high mountain lakes, and mobilizes soil aluminium. However, the focus of this discussion is ozone.

The ozone photochemistry diagram shows why hydrocarbon reduction alone as a control measure leads to less ozone exposure (illustrated by the red line 'lower HC' compared to the black line). When hydrocarbon reduction is combined with comparable NO reduction, this hypothetical control scenario results in the blue line ('lower HC and NO'). The titration segment (B) is shortened. Some areas actually develop higher ozone levels than the base case (blue line above black line). This small but important region, where the combined reduction is worse than no reduction at all, lies close to the highly populated urban region. With the combined reduction, all the inhabitants of the hydrocarbon-limited segment (C) experience higher ozone exposures than they would have experienced had the hydrocarbon reduction occurred without NO_x emission reduction (blue line above red line). The only place where anyone experiences lower ozone exposure with combined HC and NO_x reduction compared to HC reduction alone is out on the right-hand end of the diagram (far downwind, where the red and blue lines cross), assuming that the system actually gets there before the sun sets. I believe that we do not in the Denver area, nor in the Los Angeles basin.

Air quality measurements of CO, HC, and NO_x in the United States show continuous reductions over several decades. The observation of lower CO and HC—ozone precursors—would lead all interested parties to expect continued reduction in ozone concentrations. Ozone concentrations however seem to be steady or even increasing in the last few years.[5] This unexpected observation is partly explained by the discussion above which indicates that the improvement expected from the reduction in urban HC and CO emissions has been offset by the concomitant reduction in NO emissions.

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