The Weekend Effect: the science suggests that we are embarking on an expensive policy which will harm the environment

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What is the weekend effect

We know that photochemical ozone arises from emissions of hydrocarbons (HC) and oxides of nitrogen [(NOx) today mostly emitted as NO] in combination with sunlight. Every weekend there is a reduction in HC emissions (less miles driven) and a larger reduction in NOx emissions. These emissions reductions surely should cause ozone (O3) to go down. In many places ozone either goes up or remains at the same level as weekdays. In both cases this is an observation of the weekend effect.

My recommendation is that the 2010 mandatory NOx emissions reductions should be postponed until the inevitable HC emissions reductions bring ozone so far into compliance that the disbenefits of NOx reduction will be unimportant.
Elkus and Wilson, (1977) in “Photochemical Air Pollution: Weekend-Weekday Differences” stated:

In fact, we find that for most of the year the average weekend oxidant concentration is higher than the corresponding weekday value, despite the lowered emissions.

Calvert and McQuigg (1975) demonstrated, using a computer model, that increasing NOx input decreased ozone formation. The conclusion, quoted from NRC (1977) was:

These data do not mean that unrestricted emissions of NOx would solve the smog problem; however, they do imply that smog formation would be delayed. At some point downwind, the turbulent mixing will cause a reduction in the NOx level that will be loaded for smog formation.
Reason for the weekend effect

Photostationary State

\[
\begin{align*}
\text{NO}_2 + h\nu &= \text{NO} + O \quad \text{j(1)} \\
O + O_2 + M &= O_3 + M \quad \text{k(2)} \\
\text{NO} + O_3 &= \text{NO}_2 + O_2 \quad \text{k(3)} \text{ THE TITRATION REACTION}
\end{align*}
\]

\[
d\text{NO}/dt \sim 0
\]

\[
d[\text{NO}]/dt = \text{j(1)}*[\text{NO}_2] - \text{k(3)}*[O_3]*[\text{NO}]
\]

\[
[O_3] = \text{j(1)}*[\text{NO}_2]/\text{k(3)}*[\text{NO}]
\]

\[
\text{HO}_2 + \text{NO} = \text{OH} + \text{NO}_2
\]
The breakthrough in understanding the photochemistry comes from:


When time and sunshine are combined on the x-axis, the rate of ozone formation is proportional only the HC concentration and reactivity.

The amount of ozone removed when the NO is emitted and formed when the HC runs out (if the sunshine remains) is proportional only to the NOx emissions.
Ozone as a function of time in Los Angeles

Simplified ozone model

-200 -150 -100 -50 0 50 100 150 200 250 300

4:00 6:00 8:00 10:00 12:00 14:00 16:00 18:00 20:00 22:00

Time x sunlight

-200 -150 -100

Upwind ozone

Titration region

Hydrocarbon limited buildup region

NOx limited ozone maximum

Disregard negative ozone concentrations in reality they stop at zero
The benefits of HC reduction

Simplified model 25% HC reduction only

Base case

Upwind ozone same

Titration region longer

HC limited buildup slower everyone is BETTER OFF

Disregard negative ozone concentrations. In reality they stop at zero.
The disbenefits of NOx Reductions

Most people are worse off

Simplified model HC and NOx reduction

Disregard negative ozone concentrations in reality they stop at zero

Almost everyone would have been better had the NOx reduction not occurred

Upwind ozone same

Less NOx less titration

Ozone ppt.

Time x sunlight
Most everyone breathes higher weekend ozone now and in 2010 it will be worse

Simplified Model Weekend Effect 1985 and 2003

Ozone ppb

Time x sunlight

Sunset

1985

2003

weekday

weekend
If NOx is emitted as NO2 very bad things happen

Simplified model with all NOx emission as NO2

Ozone ppb

Time x sunlight
Summary and Conclusions

• Hydrocarbon reductions lead to a slower ozone buildup which is better for everyone.

• NOx reductions lessen the benefits of hydrocarbon reductions and most people are worse off.

• Most everyone breathes higher weekend ozone now and in 2010 ozone levels will be worse.

• The science suggests that current NOx reduction policies will harm the environment