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Review of

"Investigation of How Distributions of Hourly Nitrogen Dioxide Concentrations Have Changed Over Time in Six Cities" by Michael Rizzo, November 20, 2008 (EPA-HQ-OAR-2006-0922)

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Rizzo (2008) conducted a comparison of the frequency distributions of ambient hourly measurements of nitrogen dioxide (NO_2) in urban areas for recent years, when annual average NO_2 concentrations are very low and during the mid-1980s when concentrations were substantially higher. The analyses consisted of snapshots of percentile plots of the concentrations for a selected recent year and plotted against an earlier year. The contention of the assessment, as applied in the final REA, is that 1) the percentile plots generally display a linear relationship, and therefore, 2) the peak to mean ratios (as indicated by the ratio of the 98th percentile hourly NO_2 concentration divided by the average NO_2 concentration) are relatively invariant. Thus, as applied in the REA, the measured peak-to-mean ratio is used to extrapolate peak (98th percentile) NO_2 concentrations for a hypothetical state of the atmosphere where the current annual average NO_2 NAAQS is just met.

To demonstrate the degree to which the distributions are linearly related, Rizzo fit the percentile-percentile scatter plots to a straight line using regression techniques, and he also provided the square of the correlation coefficient (R^2, also referred to as the coefficient of determination). There are several flaws in the analysis that have a direct bearing on the suggested invariant nature of the peak-to-mean ratio with changing annual average NO_2 concentrations.

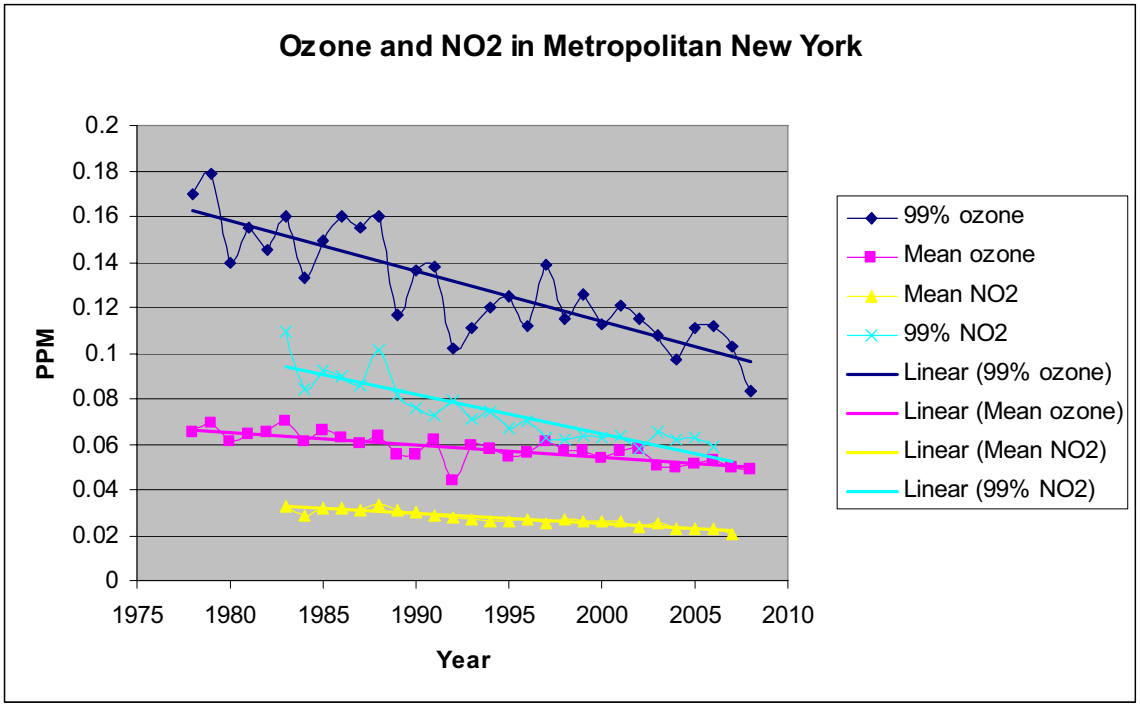
- The premise that a linear relationship between the recent and past frequency distributions is sufficient to indicate that the peak-to-mean ratio is invariant is incorrect. In order for this to be true, the distributions would need to be not only linearly related, but also proportionately related. That is, instead of a relationship of Y = a X + b, a relationship of Y = a X is required, where b = 0. Graphically, the fitted line would need to pass through the origin. The scales on the X (mid-1980s year) and Y axes (recent year) plotted by Rizzo are inexplicably shifted so that it appears that the fitted line passes through the "apparent" origin. However, since the origin of the plots are not (X=0 and Y=0), the relationships are <u>not</u> proportional. The appearance of the plots could have been corrected to the convention of an origin of (0,0) by restricting the curve fitting program to set b=0.

- Even if a proportional relationship were shown to provide a "good" fit to the data, the peak-to-mean ratio depends upon the extremes of the distribution. For example, if the middle percentile values, e.g., from 10% to 90%, fall along a line of proportionality, the R^2 value could be close to

1, but the actual peak to mean ratios (as defined above) for the two years could still be quite different from one another because the peaks are in the upper tail of the distribution.

- The analysis does not consider the atmospheric chemistry that is involved in the formation of NO_2 from NO_x emissions, comprised primarily of NO. The transformation of NO to NO_2 involves reactions with atmospheric oxidants, primarily ozone (O_3). If the peak-to-mean ratio was found to be about the same in the mid 1980s (when average NO_2 was higher) as it was in recent years (when average NO_2 is lower), it would have to be associated with consistent trends in ambient ozone concentrations.

The following figure illustrates the long-term trends of NO_2 and O_3 concentrations in the metropolitan New York City area as obtained from EPA's AIRDATA website (http://www.epa.gov/aqspubl1/annual_summary.html). The plot shows the annual average and 99th percentile values of NO_2 and O_3 decrease by about the same rate. Thus, because there was much more ozone available to convert NO to NO_2 and because NO_x emissions are primarily NO, it would be expected that the percentile-percentile plots of NO_2 for later years versus early years would show a linear relationship and that the peak-to-mean ratios would be similar. However, this assumption is not valid for the scenario in which the NO_2 concentrations approach the NAAQS because ozone concentrations are expected to be reduced in the future.



The Rizzo analysis has assumed that because the peak-to-mean ratio was relatively constant over the years, it is also appropriate to assume that it will remain constant in the future. By using proportional roll-up to project short-term NO_2 air quality to a future state where the annual standard is just attained, EPA has inherently assumed that ozone concentrations will increase commensurately. However, the recent establishment of a lower NAAQS for ozone will ensure that at most urban locations, the ambient concentrations of ozone will decrease or, in attainment areas, not increase substantially, due to controls and emissions reductions of ozone precursors (VOC and NO_x). Since the U.S. has installed VOC controls on industry, catalytic converters on vehicles and vapor recovery at gas stations, it is inconceivable that ozone will be allowed increase in the future.

Based on these factors, the Rizzo analysis is incomplete and results in misleading conclusions as to whether the peak-to-mean ratio is invariant as applied to the flawed simple roll-up calculation for the case of just meeting the current annual NAAQS.

In summary, a demonstration is made in the final REA and in the November 20, 2008 Rizzo memo that the frequency distribution of 1-hour NO_2 concentrations does not change from a low concentration year (present day) to a high concentration year (mid 1980's). EPA's premise that a linear relationship between the distributions from one year to another is sufficient to validate constant peak to mean ratio is only partially correct in that that a proportional relationship is required. The scales on the axes of the figures in the REA and the memo are adjusted such that the relationship appears to be proportional, but the best-fit line does not pass through the conventional origin of (0,0). More importantly, the reason that the peak-to-mean ratios do not appear to change much from the high year to the low year is that over this period, the ambient ozone, which governs the formation NO_2 from NO emissions, has also decreased over time. Thus, in using the roll-up method, EPA has assumed that the ambient ozone will increase to historically high levels. This is in direct conflict with maintenance of the ozone NAAQS and impossible unless VOC emissions, which have decreased dramatically over the past decades, also increase along with NO_x.