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*Secretary for Environmental Protection*

# Air Resources Board

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Gray Davis
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MEMORANDUM

TO: Peter Venturini, Chief
Stationary Source Division

FROM: Terry McGuire, Chief
Planning & Technical Support Division

DATE: January 19, 1999

SUBJECT: ATMOSPHERIC CONDITIONS WHICH FAVOR NEGATIVE HYDROCARBON REACTIVITY

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Attached is a paper entitled *$NO_x$ Concentrations and VOC/$NO_x$ Ratios in California* which discusses the Dunn-Edwards issue regarding negative hydrocarbon reactivity.

This paper affirms that Dunn-Edwards is correct in that when $NO_x$ concentrations are very low and VOC/$NO_x$ ratios are very high, many hydrocarbons exhibit negative reactivities. The paper goes on to examine recent prevailing air quality conditions in the California air basins which experience ozone problems and finds that such $NO_x$ and VOC/$NO_x$ conditions are almost non-existent.

If you have questions regarding this matter, please contact Luis Woodhouse at 322-6156.

Attachment

cc: Luis Woodhouse

# $NO_x$ Concentrations and VOC/$NO_x$ Ratios in California

**January 19, 1999**

## Introduction

Dunn-Edwards Corporation (DEC) has provided the California Air Resources Board (CARB) with the results of research conducted by Dr. William Carter, using box-model simulations and the SAPRC-97 chemical mechanism. The research looked at the influence of nitrogen oxide ($NO_x$) concentrations on the incremental reactivity (IR) of selected volatile organic compounds (VOCs). The VOCs studied were n-octane, ethanol, m-xylene, toluene, and an urban ROG mixture. The $NO_x$ concentrations used in the research ranged from 1 ppb up to 40 ppb, with the VOC/$NO_x$ ratios of up to 80. Dr. Carter showed that as the $NO_x$ concentration is reduced, or, equivalently, as the VOC/$NO_x$ ratio increases, the reactivity of the VOCs decreases and can become negative. This research also shows that as $NO_x$ increases the IR will increase and eventually become positive for all VOCs studied. However, note that the chemical mechanism used in the DEC study has not been adequately evaluated at these low $NO_x$ concentrations (Carter, 1998).

The DEC study confirms that the IR of organic compounds depends on the environmental conditions, particularly on $NO_x$ availability. For example, when the initial $NO_x$ concentration is 20 ppb, m-xylene shows negative IRs at VOC/$NO_x$ ratios of 30 and above. When the initial $NO_x$ concentration is 5 ppb, m-xylene shows negative IRs at VOC/$NO_x$ ratios of 40 and above. Toluene, n-octane and the Urban ROG mixture show negative IRs at lower VOC/$NO_x$ ratios. At 1 ppb or less of initial $NO_x$, all VOCs studied, except ethanol, had negative IRs at all VOC/$NO_x$ ratios.

The data conclusions by DEC are based on sound scientific research and agree with the results of other research (Carter *et al.*, 1994), confirming the IR dependence on the VOC/$NO_x$ ratio, and showing that at very low $NO_x$ concentrations the IR can become negative as the VOC/$NO_x$ ratio increases. At low $NO_x$ concentrations, the removal of $NO_x$ by reactions with VOCs to form nitrogen-containing products become very important and can have negative effects on the formation of ozone. In addition, at very low $NO_x$ concentrations, radical-radical termination reactions will be enhanced which will retard the generation of ozone (Bergin, *et al.*, 1998).

## Ambient NMOC/$NO_x$ Ratios

Ambient NMOC/$NO_x$ ratios (NMOC stands for nonmethane organic compounds) are calculated using data collected in the early morning, 6-9 a.m., of a given day. This ratio is an indicator of the ambient ozone precursors before the photochemical reactions that generate smog take place, and it is similar, in concept, to the initial NMOC/$NO_x$ ratio that is used to characterize a smog chamber before the start an experiment (i.e., before the air sample is irradiated). However, the 6-9 a.m. NMOC/$NO_x$ ratio does not represent the complexities of ozone formation, such as the effect of pollutant transport, in California

air basins. We used air quality data obtained from the Photochemical Assessment Monitoring Stations, PAMS, to calculate 6-9 a.m. NMOC/$NO_x$ ratios in California. The PAMS monitoring network provides for improved sampling procedures, better data quality control, and, also, speciation of NMOC. Data used in this analysis were from the summers of 1996 and 1997 (the most recent data available after the statewide introduction of cleaner burning gasoline), and they are summarized in Tables A and B for selected sites.

According to the information provided by DEC, the Urban ROG mix, which is used to represent ambient air in smog chamber experiments, had a negative reactivity at a NMOC/$NO_x$ ratio of 20 or greater, and $NO_x$ concentrations between 5-40 ppb. We calculated the percent of ambient air samples that had both a $NO_x$ concentration of 40 ppb, or less, and a NMOC/$NO_x$ ratio of 20, or greater, and they are summarized in Table C.

The information shown in Tables A, B, and C demonstrate that the $NO_x$ concentrations and NMOC/$NO_x$ ratios used in the DEC study are not typical of the ambient conditions of California. For example, during the summers of 1996 and 1997, the average NMOC/$NO_x$ ratio is below 15 for all the sites studied. The percent of samples that had a $NO_x$ concentration of 40 ppb, or less, and a NMOC/$NO_x$ ratio of 20, or greater, is 0 to 4 percent at most sites. The monitoring stations in Sacramento Del Paso Manor and Arvin had only 10 percent of the samples with ratios over 20, together with a $NO_x$ concentration of 40 ppb, or less. The Los Angeles North Main Street monitoring site, situated in the air basin with the worst pollution problem in California, had an average NMOC/$NO_x$ ratio of about 5, with the maximum ratio not exceeding a value of 10.

## Conclusions

The data presented by DEC is based on sound scientific research, however, air quality typical of California shows that $NO_x$ concentrations are dramatically greater and NMOC/$NO_x$ ratios are almost always lower than those that result in negative IRs.

## References

Bergin, M. S., A. G. Russell, W.P.L. Carter, B. E. Croes, and J.H. Seinfeld, "*VOC Reactivity and Urban Ozone Control.*" Encyclopedia of Environmental Analysis and Remediation, 1998.

Carter, W.P.L. D. Luo, I. L. Malkina, and J. A. Pierce, "*Environmental Chamber Studies of Atmospheric Reactivities of Volatile Organic Compounds. Effects of Varying ROG and $NO_x$.*" Final Report to Coordinating Council, Inc., California Air Resources Board, South Coast Air Quality Management District. September 10, 1994.

Carter, W.P.L., personal communication to L. Woodhouse (November, 1998).

**Table A**
**NMOC to $NO_x$ Ratio (6-9 AM) from Selected Sites in California**
**(Summers 1996 and 1997)**

| Site | Average | Minimum | Maximum | Std. Dev. |
|---|---|---|---|---|
| Fresno –1st Street | 6.2 | 3.5 | 13.6 | 2.0 |
| Parlier | 6.4 | 3.7 | 14.3 | 1.8 |
| Clovis –N Villa Avenue | 8.6 | 3.0 | 100.7 | 12.0 |
| Bakersfield –Golden State Hwy | 6.9 | 3.0 | 19.4 | 2.6 |
| Arvin –Bear Mountain Blvd. | 14.8 | 2.6 | 243.3 | 33.6 |
| Los Angeles –North Main Street | 4.6 | 1.6 | 9.5 | 1.8 |
| Sacramento –Del Paso Manor | 13.7 | 3.8 | 160.5 | 22.5 |
| Elk Grove –Bruceville Road | 7.9 | 1.7 | 35.4 | 5.9 |
| Folsom –Natoma Street | 7.8 | 2.0 | 20.4 | 4.0 |
| San Diego –12th Street | 7.7 | 2.2 | 35.3 | 6.3 |

**Table B**
**$NO_x$ Concentrations[a] (6-9 AM) from Selected Sites in California**
**(Summers 1996 and 1997)**
**-ppb-**

| Site | Average | Minimum | Maximum | Std. Dev. |
|---|---|---|---|---|
| Fresno –1st Street | 49 | 11 | 140 | 29 |
| Parlier | 31 | 13 | 53 | 10 |
| Clovis –N Villa Avenue | 36 | 8 | 102 | 18 |
| Bakersfield –Golden State Hwy | 69 | 16 | 142 | 32 |
| Arvin –Bear Mountain Blvd. | 20 | 5 | 54 | 10 |
| Los Angeles –North Main Street | 145 | 15 | 325 | 95 |
| Sacramento –Del Paso Manor | 25 | 1 | 95 | 20 |
| Elk Grove –Bruceville Road | 17 | 2 | 47 | 12 |
| Folsom –Natoma Street | 17 | 4 | 38 | 9 |
| San Diego –12th Street | 45 | 6 | 170 | 33 |

a) Data for this table corresponds to days with available NMOC data. Data for days with no NMOC were not included

**Table C**
**Percent of Samples (6-9 a.m.) with**
**Ambient $NO_x$ Concentration Less Than or Equal to 40 ppb,**
**and NMOC/$NO_x$ Ratio Greater Than or Equal to 20**
**For Selected Sites in California**
**(Summers of 1996 and 1997)**

| Monitoring Site | Percent |
|---|---|
| Fresno –1st Street | 0 |
| Parlier | 0 |
| Clovis –N Villa Avenue | 2 |
| Bakersfield –Golden State Hwy | 0 |
| Arvin -Bear Mountain Blvd. | 10 |
| Los Angeles –North Main Street | 0 |
| Sacramento –Del Paso Manor | 12 |
| Elk Grove –Bruceville Road | 4 |
| Folsom –Natoma Street | 3 |
| San Diego –12th Street | 4 |