AN OBSERVATIONAL INVESTIGATION OF OZONE SENSITIVITY TO VOC AND NOx AND ITS VARIATION IN THE HOUSTON-GALVESTON-BRAZORIA (HGB) OZONE NON-ATTAINMENT AREA[1]

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Background and Purpose

This investigation was undertaken in support of TCEQ's high-priority SIP-Relevant Questions F and K. One of the authors (BD) had proposed to TCEQ a modeling study for answering Question F. That proposal was for a fairly large effort to model ozone production in the HGB area during an extended period of time using a grid model equipped with DDM sensitivity analysis software. That proposed study, however, could not be included in the Second Texas Air Quality in 2005-2006. This prompted us to undertake a modest effort for the specific purpose of assessing **through use of observational data** the utility of evidence on variation of ozone sensitivity to NOx and VOC within the HGB ozone non-attainment area, and thereby to assess the justification of Question F and the need for conducting comprehensive modeling or observational studies to answer that Question.

The limited effort that could be spent on this investigation and the less-than-sufficient observational data available did not allow development of a full-fledged observational method ready to use for characterizing the ozone-to-precursors sensitivity within the HGB area. The present effort, therefore, focused on development of an approximate method that nevertheless would produce pertinent and reasonably conclusive evidence with respect to the intended purpose of assessing the utility of ozone sensitivity evidence.

Observational Approach and Procedures

The observational approach conceived and used in this effort is one based on use of commonly obtained observations on ambient VOC and NOx conditions. Two key features of the approach are, first, the need for a very extensive data base, i.e., extensive in terms of number of days and number of sites within HGB, and, second, the use of a chemical mechanism model. These two requirements are discussed next, starting with the data requirement.

The specific observational data required by the approach are data on ambient VOC/NOx-ratio and VOC-composition conditions during early morning hours -- the hour of 8:00-9:00 AM was used here. Such data are available in abundance for HGB, and, therefore, such data will be used for describing the approach and illustrating its application and the type of evidence it produces.

The ambient VOC/NOx ratio and VOC composition conditions were selected for use here because these two conditions represent **the** emissions-related factors that determine the sensitivity of ozone to its two precursors. These two conditions vary widely, both, spatially and temporally, within HGB, and, as a consequence, the ozone sensitivity also is thought to vary widely in HGB. That the VOC/NOx ratio and VOC composition conditions within HGB vary widely is well known, but there is no specific and detailed evidence on how widely the **ozone sensitivity** varies. Does it vary only from more VOC-limited to less VOC-limited or from more NOx-limited to less NOx-limited, or does it vary drastically, that is,

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from VOC-limited to NOx-limited and vice versa. And if the HGB area experiences both VOC-limited and NOx-limited ozone exceedances, can all exceedances be prevented by combined VOC and NOx controls? Before answering these questions, it is necessary that the reasons for the variation of the precursor conditions first be discussed in some detail.

There are good reasons why the VOC/NOx ratio and VOC composition conditions and ozone sensitivity should vary widely in HGB. The HGB area is impacted by five types of ozone-precursor emissions, which, because of their large amounts and widely different reactivities with respect to producing ozone, and, also, because they are unevenly distributed spatially and temporally within HGB, they have strong and potentially very different and widely varying effects on ozone production in HGB. These five types of emissions are:

(a) highly reactive industrial VOC emissions (HRVOC) -- mostly olefins and diolefins – from petrochemical industry sources located mainly in the industrial Ship Channel area within the eastern part of HGB,

(b) anthropogenic VOC emissions, other than HRVOCs, mainly from mobile sources and other ordinary-urban-area sources, occurring throughout the HGB area,

(c) biogenic, -- also highly reactive -- VOC emissions from sources located both within the urban centers and in the forest mainly north and west of Houston,

(d) mobile source NOx emissions occurring throughout the HGB area, and

(e) industrial NOx emissions from sources located both within the urban centers and in the industrial sections of HGB.

Thus, the emission picture in HGB is one in which a blanket of mobile-source emissions covers the entire HGB area, upon parts of which blanket are superimposed, to different extents during different times, **depending mainly on wind conditions**, the industrial and biogenic emissions. Such a picture logically suggests that **t**he ambient VOC/NOx ratio and VOC-composition conditions within HGB should vary widely, both, spatially, and temporally. It also suggests, in consequence, that, in order to establish the variation of ozone sensitivity in HGB, it will be necessary to obtain data covering the entire spectrum of ambient VOC/NOx ratio and the VOC composition conditions in HGB. To ensure this, requires that the HGB atmosphere be monitored for these two conditions for a long period of time, and at as many sites as possible. In short, it is for this reason that this observational approach requires use of observations from many HGB sites and for an extended period of time.

With respect to the need for a mechanistic model, such a model is needed because it offers the only method by which the VOC/NOx-ratio and VOC composition conditions can be translated into ozone sensitivity. In this effort, the mechanistic model selected was the Empirical Kenetic Modeling Approach (EKMA) model, more specifically the version that takes into account the time-varying post-8AM anthropogenic VOC and NOx and biogenic VOC emissions, and applied it to relate the 8AM ambient concentrations of VOC and NOx and VOC composition to the day's peak 8-hr ozone concentration. There are two aspects of the procedure by which EKMA was used that need discussion: One is the definitions used of "NOx-limitation" and "VOC-limitation," and the other is the procedure used for constructing the requisite EKMA diagram.

The definitions of "VOC-limitation" and "NOx-limitation" used here are different from the traditional ones. By the traditional definitions, VOC-limited conditions are those associated with VOC/NOx ratios below that of the "equal effectiveness" ratio, i.e., the ratio represented by the line OZ in Figure 1, and NOx-limited conditions are those associated with ratios higher than that of the OZ line. One effect to remember, as we will refer to it later, is that the effectiveness of VOC control decreases with decreasing NOx concentrations

or increasing VOC/NOx ratios. Also, it should be understood that the traditional definitions do not imply that under VOC-limited or NOx-limited conditions ozone exceedances can be prevented **only** through VOC control or **onl**y through NOx control, respectively. In fact, under either type of conditions, ozone exceedances can be prevented either through VOC control or through NOx control, but the control requirements are different.

For the purposes of this investigation, and for reasons that will become evident later, the definitions used are different than the traditional ones. Specifically, as defined here, "NOx-limited" precursor conditions are those conditions which are conducive to ozone exceedances but which exceedances cannot be prevented through anthropogenic VOC control, even 100% control. Such conditions, for example, occur when the biogenic VOC emissions alone can cause ozone exceedances. In turn, VOC-limited conditions are defined to be all those conditions that are not NOx-limited, that is, conditions conducive to exceedance, but which exceedances can be prevented through control of either VOC or of NOx or of both.

The procedure for constructing the requisite EKMA isopleth diagram is illustrated by using Harris County as the study area. The diagram was constructed by using

(i) a "typical" Harris County VOC mix, based on measurements at the LaPorte site,

(ii) a constant 30-ppb concentration of ozone entrained aloft,

(iii) time-varying post-8AM VOC and NOx emissions,

(iv) time-varying post-8AM isoprene emissions estimated from the tons per day of isoprene emitted in Harris County, the area of Harris County, and data on the time-variation of isoprene emissions estimated from the BEIS model, and

(v) a typical time-varying mixing height based on measurements made at the Moody Tower site.

Finally, in order also to take into account: a) increases in biogenic VOC concentrations caused by higher than average temperatures, b) increases due to transport of biogenic VOCs into Harris County, and c) the fact that isoprene alone under-represents the total biogenic VOC, the isoprene emissions input during the post-8AM hours was increased by a factor of 2.

Results

The resultant EKMA diagram, shown in Figure 2, is the one used to translate the 8AM VOC and NOx observations into ozone sensitivity. This translation was achieved as follows:

For each set of 8AM concentrations of VOC and NOx, we established, based on the EKMA diagram, whether these concentrations reflect ozone exceedance conditions, and, if they do, whether the ozone exceedance is VOC-limited or NOx-limited by the definitions used here. Thus, point A represents NOx-limited exceedance conditions, point B represents VOC-limited exceedance conditions, and points C represent non-exceedance conditions. This led us to determine for each ozone monitoring site, the fraction of ozone exceedance days (during the 2005 and 2006 smog seasons) during which days the precursor conditions were conducive to producing NOx-limited ozone exceedances. For illustration purposes, such fractions were derived for five HGB monitoring sites, all within Harris County, and for all days during the 2005 and 2006 smog seasons. The resulting fractions of all expected ozone exceedance days that were NOx limited were: 54% for Clinton, 17% for Channel View, 35% for Wallisville, 39% for Lynchburg Ferry, and 43% for HRM-3

Interpretation of Results and Conclusions

First, it is noted that the key evidence targeted by this investigation is, specifically, evidence on whether or not precursor conditions causing NOx-limited ozone exceedances in HGB occurred in 2005 and 2006 with significant frequency. The reason for interest in such evidence is that if such conditions **do not** occur within the non-attainment area with significant frequency, it will have to be concluded that the optimum control strategy for that area should be control of VOC or an optimum combination of VOC and NOx controls throughout the non-attainment area. If, on the other hand, NOx-limited conditions **do occur** in the non-attainment area with significant frequency, then, given that such exceedances cannot be prevented through VOC control, however intensive such control may be, it will have to be concluded that **NOx control in that area is imperative**. The results from our investigation point to this latter case for Harris County.

The significantly frequent occurrence of NOx-limited exceedance conditions in Harris County suggests that NOx control in this county is imperative for preventing such exceedances. But, Harris county also experiences VOC-limited exceedances, and this is a problem that also needs to be dealt with. There are, conceivably, two alternative control strategies for dealing with this problem. One is, simply, to apply NOx control drastic enough to prevent all exceedances -- both NOx-limited and VOC-limited ones. The other alternative is to apply both NOx controls and VOC controls, the latter tailored for preventing the VOC-limited exceedances. There is a serious problem with this second strategy, however. As alluded to above, the NOx control dictated by the NOx-limited exceedances raises substantially the degree of VOC control needed for preventing the VOC-limited exceedances. In the face of this problem, therefore, it will have to be concluded **that the first alternative, that is, drastic NOx control strategy may be the optimum control strategy for achieving ozone attainment throughout the Harris County area.** This, of course, does not mean discounting the need for VOC controls. It merely means that such need must be justified on non-ozone bases.

As a final comment, it is stressed once again that the results and conclusion from this investigation should be viewed only as an illustration of the kind of ozone-sensitivity evidence needed and the relevance and value of such evidence. Nevertheless, the authors also submit that application of the observational approach described here in a comprehensive study, that is, a study that utilizes observational data on ambient VOC and NOx concentrations and VOC composition at all HGB monitoring sites, and for a period of 2-3 smog seasons, should provide fairly reliable answers to TCEQ's high-priority SIP-relevant Questions F and K.

At a minimum, the findings from this limited investigation indicate the validity and importance of TCEQ's Question F and the urgent need for a comprehensive modeling or observational study to answer that Question.

The authors of this paper are very interested to receive comments or questions about any aspects of this study. The authors can be contacted at basildi@hotmail.com and luecken.deborah@epa.gov

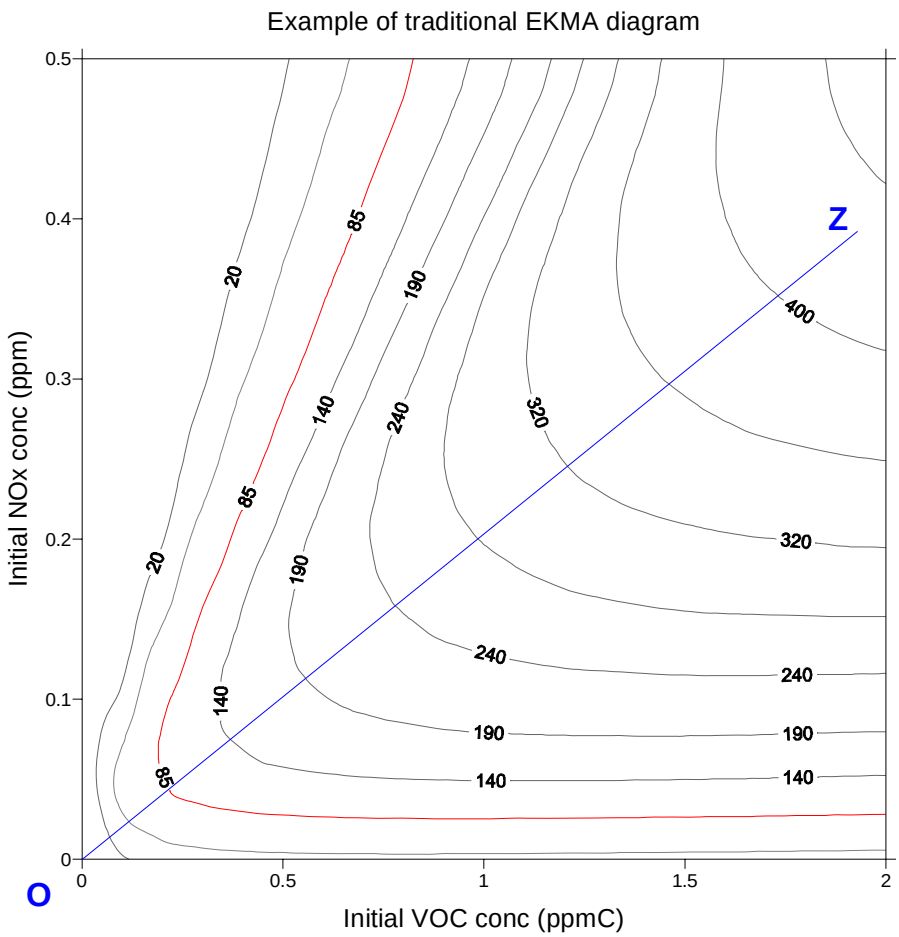

Figure 1. EKMA Ozone Isopleth Diagram

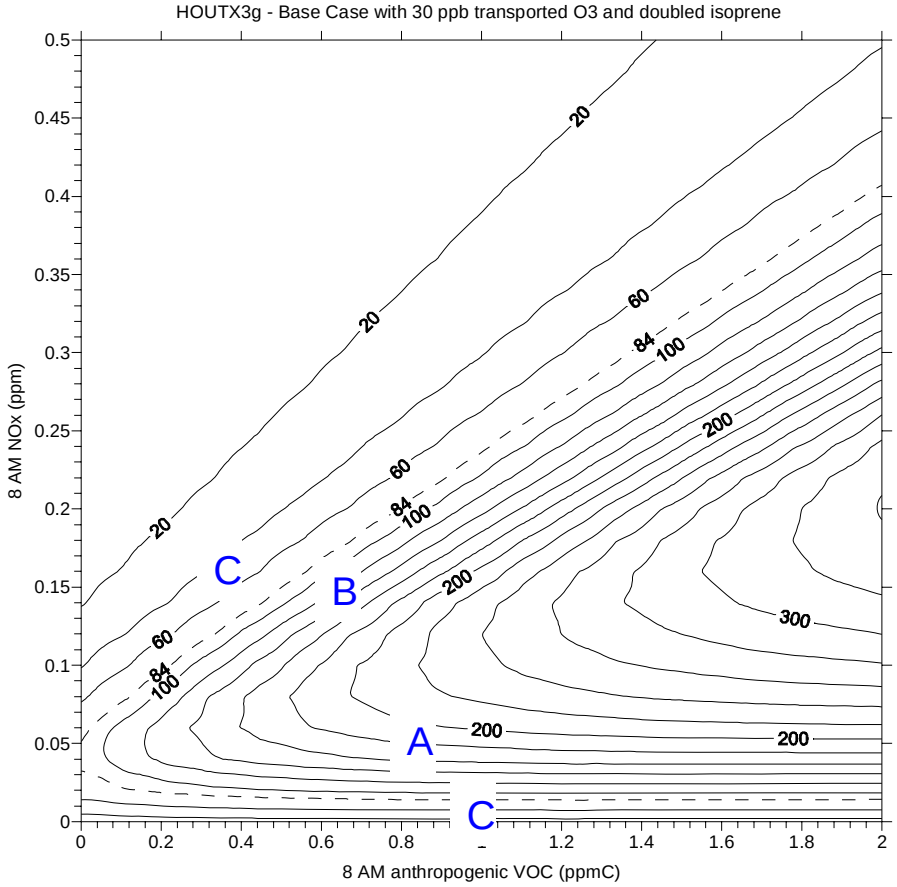

Figure 2. EKMA Ozone Isopleth Diagram for Harris County