

CHAPTER 4

OBSERVATIONAL BASED METHODS FOR DETERMINING VOC/NO_x EFFECTIVENESS

4.1 INTRODUCTION

Observational based models (OBMs) represent a broad group of data analysis techniques, subject to many descriptions regarding their formulations and applications. Perhaps the distinguishing feature of OBMs is that they are driven principally by observed (or ambient) data as opposed to grid models which are driven by emissions estimates. Observational analysis methods include receptor models, regression techniques, ambient ratios (e.g., VOC/NO_x), indicator species and the more semi-empirical based OBMs. This chapter is restricted to those methods which are capable of inferring control strategy effectiveness (e.g., NO_x or VOC control preference). Source attribution and related methods for assessing emissions inventories are covered in Chapter 3.

This chapter follows a method (or method class) by method approach, starting with highly empirical¹ ratio techniques and proceeding to the more semi-empirical OBMs which incorporate some degree of mechanistic-based chemistry formulations. All of the techniques discussed require “routine” data sources comparable to that available from a PAMS network, with certain exceptions in NO_x measurements. Each methodology section provides case examples taken from the literature or developed from available data sources.

4.2 EMPIRICAL TECHNIQUES

4.2.1 VOC/NO_x Ratios

Ratios based on the concentrations of VOC to NO_x have been used for relating emission inventories to ambient data, as well as delineating NO_x and VOC control requirements. Generally, the propensity of an area to be VOC- or NO_x-limited is based on the measured (or predicted) ratio. Higher and lower ratios imply NO_x- and VOC-limiting conditions, respectively. No specific cutoff ratios exist, since whether ozone formation is limited by VOC or NO_x depends on other factors in addition to the VOC/NO_x ratio. However, for the conditions often assumed in EKMA/OZIPM4 ozone isopleth diagrams ratios greater than 16 often were considered NO_x-limited and ratios less than 6 were considered VOC-limited (U.S. EPA, 1989). The VOC/NO_x ratio technique is based on well understood atmospheric chemistry processes, and represented in

¹ All approaches have logical foundations in, or their behavior can be explained by, atmospheric chemistry principles.

ozone isopleth diagrams (Figure 4-1) derived from photochemical “box-type” models such as EPA’s EKMA/OZIPM4 (U.S. EPA, 1989).

As part of the evaluations of 1993 PAMS data from three sites in Houston, Texas and Baton Rouge, Louisiana, ratios were calculated from three hour averages of TNMHC and NO_x , and TNMHC and CO for the three PAMS sites². The summary statistics for the ratios are presented in Table 4-1 (Stoeckenius et al., 1994). For Houston, the TNMHC/ NO_x ratios were found to be higher at the Clinton Drive than at the Galleria site, as might be expected given the dominance of petrochemical industry sources at Clinton Drive. The ratios at the Baton Rouge site are lower than at either Houston site. In contrast, morning (6–9 a.m.) ratios are very similar at all three sites. The Clinton site appears subject to higher evaporative emissions and fewer NO_x sources during the day as compared to Galleria or Capitol.

Relationships between morning TNMHC/ NO_x ratios and daily maximum ozone concentrations may provide insight into the potential tradeoffs between VOC and NO_x control strategies. Scatter plots of 6–9 a.m. TNMHC/ NO_x ratios with daily maximum ozone concentrations observed within the Houston non-attainment region and daily maximum temperature (as measured at the PAMS site) are presented in Figures 4-2 and 4-3 (Stoeckenius et al., 1994). At these sites, ozone concentrations above 0.10 ppm are associated exclusively with TNMHC/ NO_x ratios less than about 10. There is some hint in these data that the TNMHC/ NO_x ratio decreases with increasing ozone concentrations above 0.10 ppm. If this is confirmed by further analysis, it would suggest that Houston is in a NO_x limited regime.

Nearly all of the TNMHC/ NO_x ratios above 10 at the Houston sites are associated with maximum ozone values substantially below 0.10 ppm. TNMHC/ NO_x ratios substantially above 10 may be associated with older air masses with very low NO_x concentrations and a lower proportion of reactive NMHCs³. This could be confirmed by further analyses comparing the reactivity weighted TNMHC on days with different TNMHC/ NO_x ratios and a more detailed examination of meteorological conditions. Figures 4-2 and 4-3 suggest that the meteorological conditions that place these aged air masses over the Houston site on certain mornings are not conducive to the formation of high ozone concentrations in the Houston area (Stoeckenius et al., 1994). As is typical of most urban areas, the daily maximum ozone concentrations in Houston are related to the daily maximum temperature with the highest ozone found on the warmest days. There are no obvious relationships between maximum temperature and 6 to 9 a.m. TNMHC/ NO_x ratios.

²Ratios were set to missing for 3-hour blocks with two or more missing TNMHC or NO_x concentrations.

³High TNMHC/ NO_x ratios may also be associated with very low NO_x concentrations that are not accurately measured. Investigation of this possibility was beyond the scope of the present study but must be conducted before any final conclusions can be drawn regarding the conditions leading to high TNMHC/ NO_x ratios.

While the VOC/NO_x method is theoretically sound, application of the technique has several limitations:

1. Historically, applications have relied upon morning, center-city VOC and NO_x measurements, yet the ratio varies widely in time and space. PAMS improves the spatial and temporal coverage of data, and therefore tempering this particular concern.
2. Assuming only limited measurement-related difficulties, the ratios delineating NO_x and VOC-limited regimes vary with time and location, and are affected by vertical mixing processes that often are not accounted for in surface measurements. Additionally, the prevailing atmospheric chemistry (e.g., composition and age of air mass) can impart different control responses at the same VOC/NO_x ratios.
3. Inconsistent and uncertain measurement techniques affect the ratio. These include various interpretations of total NMOC, measurement uncertainties and artifacts in NO_x and NMOC, and the representativeness of observations (this latter issue is more problematic for emission inventory evaluation).

By themselves, VOC/NO_x ratios probably cannot be used unambiguously to infer NO_x or VOC control strategy effectiveness. However, in combination with other observational (and gridded models) techniques, the VOC/NO_x method adds corroborative value.

4.2.2 Reactive (oxidized) Nitrogen (NO_y, NO_z) and Ozone Correlation Techniques

Several correlations relating ozone production to total oxidized nitrogen (NO_y) or NO_z (NO_y - NO_x) have been suggested as tools capable of implying VOC/NO_x control effectiveness, as well as relative air mass aging. These correlations (e.g., Figure 4-4, Olszyna et al., 1994) are generally based on large quantities of averaged data covering multiple days, and limited to the midafternoon time period (1 - 5 pm).

NO_z typically correlates better with ozone than NO_y. This may reflect ozone scavenging by one of the NO_y species (NO). Progressively higher slopes, $\Delta O_3/\Delta NO_z$, reflect NO_x limited regimes and negative or near zero slopes reflect VOC limiting conditions. The existing studies do not provide sufficient guidance to delineate clearly the range of slopes depicting NO_x or VOC limiting regimes, although slopes greater than 8 appear to suggest NO_x-limiting conditions. By themselves, the NO_z-O₃ correlation does not provide a reliable NO_x-VOC-limiting indicator. However, in combination with other observational approaches and photochemical modeling, the correlation can provide corroborative support for evaluating control effectiveness. Future applications with emerging data bases and cross analysis-method comparisons should provide

greater understanding of the utility of these correlation methods. Additional discussion on these techniques is found in Appendix A.

4.3 OBSERVATIONAL MODELS

The two semi-empirical OBMs discussed here, the Mapper-Smog Production Algorithm (SPA) and the Georgia Institute of Technology (GIT) model, rely on some level of mechanistic description of atmospheric chemistry (relative to correlation techniques) or produce explicit VOC and NO_x control effectiveness results and therefore are distinguished from other indicator and correlation techniques.

4.3.1 Smog Production Algorithm - MAPPER program

Figure 4-5 provides an example of MAPPER-SPA results. The map provides a visually-oriented time and space perspective of NO_x- (or VOC-) limitation. The circular elements are clocks reflecting hourly data at the monitoring site, the size of the diameter is in proportion to the maximum daily ozone observed at the site. Shading gradations are used to reflect extent, E, which is an indicator for degree of NO_x-limitation. Filled black reflects full extent of 1, situations clearly NO_x-limited; white reflects VOC limiting conditions with E < 0.5; and cross-hatched areas could be considered borderline NO_x-sensitive. The example is only illustrative, the shading forced to illustrate a full range of NO_x- and VOC-limiting conditions. Displays such as these can be used to corroborate control strategy results from gridded ozone models. Due to the potential for compensating errors, typical model evaluations limited to comparisons between observed and simulated concentrations do not necessarily provide confidence in the model's response to emissions perturbations. The use of OBMs which rely on observations provide a unique corroborative check on the directional ability of EBMs to respond to emissions changes.

Description

The Smog Production Algorithms (SPA) and associated MAPPER software were derived from the Integrated Empirical Rate (IER) model of Johnson (1984) and later developed by Blanchard et al. (1994). The original IER was based on smog chamber experiments in Australia. Johnson (1984) defined smog produced (SP) as:

$$SP(t) = O_3(t) - O_3(0) + NO(0) - NO(t)$$

In simple terms, SP represents the cumulative oxidation of initial NO into ozone and other oxidized "smog" products (i.e., NO_y species), presumably accounted for in the change in NO over time. With sufficient NO, SP exhibits a linear relationship with cumulative light flux until a maximum, SP_{max}, is reached. Over much of this linear period, SP can be thought of as being

VOC-limited. This maximum is related to initial NO_x in the system by,

$$\text{SP}_{\max} = \beta[\text{NO}_x(0)],$$

where the parameter, β , was assumed to be a constant of 4.1 based on the chamber experiments and reflects the potential maximum amount of smog produced per unit of NO_x input. An extent of Reaction, E, is defined as:

$$E(t) = \text{SP}(t) / \text{SP}_{\max}$$

where the extent, E, represents the fractional movement toward maximum smog production. When the extent =1, virtually all the NO_x in the system has been transformed to ozone and oxidized NO_x products (NO_z) and the system is NO_x limited. Recalling that the linearized region of $\text{SP}(t)$ is associated with VOC-limiting conditions, the value of E can be interpreted as rough indicator of VOC or NO_x -limiting conditions. That is, E with values very near or equal to 1 clearly reflect NO_x -limiting conditions, and values of E far less than 1 (say less than .5) suggest VOC limiting conditions. Thus, the derivation of equations and associated algorithms which utilize measurements as independent variables directed toward the calculation of E forms the basis for MAPPER in delineating NO_x and VOC limiting conditions. Details on the derivations and algorithms for E are found in Blanchard et al. (1994). More recent forms for SP include:

$$\text{SP}(t) = \text{O}_3(t) + \text{DO}_3(t) - \text{O}_3(0) + \text{NO}(0) - \text{NO}(t),$$

and

$$\text{SP}_{\max} = \beta[\text{NO}_x(0)]^\alpha$$

where the term $\text{DO}_3(t)$ accounts for the cumulative ozone lost to deposition from time zero to t (i.e., ozone that has been produced but deposited), and is parameterized as a function of observed ozone. Default values for β (19) and α (.67) are empirical coefficients derived from numerous smog chamber studies.

Measurement Requirements/Relation to PAMS

MAPPER algorithms require hourly measurements of ozone, NO and either NO_x or NO_y , depending on the form of the MAPPER algorithm selected. Where available, true NO_x or true NO_y data should be used in MAPPER applications. The scarcity of such data will drive many applications toward routine NO_x data. Since MAPPER operates in true NO_x and true NO_y modes and many of the available routine NO_x overestimate afternoon NO_x , the technique can provide a "bounding" associated with the positive NO_x measurement biases. In addition, PAMS locations generally are weighted toward urban core areas and the results from PAMS alone are likely to be skewed toward the urban perspective, which in many cases will infer a VOC limiting

case.

4.3.2 GIT Model

The Georgia Institute of Technology (GIT) OBM (Cardelino and Chameides, 1995) utilizes most of the data (speciated NMOC and NO_x) generated from a PAMS. The GIT-OBM quantifies the relative roles of various emission groups (e.g., natural and anthropogenic VOC, NO_x) on ozone production. Figure 4-6 illustrates a GIT-OBM application for Atlanta covering several monitoring locations.

Description⁴

Cardelino and Chameides (1995) describe the use of a box model for calculating the sensitivity of ozone to VOC or NO_x reductions, which they name the “Observation-Based Model” and is referred to here as the “GIT-OBM”. The model is an OBM because it uses ambient concentrations rather than emissions estimates to drive the calculations. The calculation is carried out separately for each monitoring location. Unlike a trajectory model, each box is fixed at the location of its monitor. The OBM utilizes some features of the OZIPM4 model to account for dilution and employs a modification of the CBM-4 (Cardelino and Chameides, 1995).

Cardelino and Chameides (1995) define a quantity, $P_{\text{O}_3\text{-NO}}^{\text{S}}$, which is the net ozone formed plus the net NO consumed over a 12-hour period (this quantity is similar to SP of the IER model but is computed as an integral over time rather than an instantaneous concentration). The fractional change in $P_{\text{O}_3\text{-NO}}^{\text{S}}$, divided by the fractional change in the “source strengths” of precursors, are used to define relative incremental reactivities (RIRs). For each measured species, instantaneous source strengths are calculated from the measurements and from production and loss terms. The RIRs for each site are (or can be) averaged to generate area-averaged RIRs. Cardelino and Chameides (1995) sum RIR terms so as to yield RIRs for NO, anthropogenic hydrocarbons (AHC), and natural hydrocarbons (NHC). The split between RIR-AHC and RIR-NHC is accomplished by summing RIRs for species arising from anthropogenic and biogenic emissions, respectively.

Limitation/Caveats

Numerous assumptions are made in the procedure. Some of the assumptions that appear to have a potentially substantial effect on the calculations are provided in Dmerjian et al. (1995) who suggest a potential bias toward overestimating the benefits of anthropogenic NO_x reductions.

1. Nature and levels of uncertainty associated with the method. Analyses of uncertainty have not

⁴This description as well as the section discussing limitations and caveats of the GIT-OBM are taken from a review of OBMs conducted by Demerjian et al. (1995).

been carried out for the OBM. Taking into account the uncertainties deriving from factors such as those listed in the preceding section, as well as the inaccuracies and unavailability of data for typical nonattainment cities, there is a clear need to quantitatively characterize the resulting overall uncertainties in the model output. At present, some of the assumptions appear to generate biases that would enhance the apparent benefits of controlling anthropogenic NO_x .

2. The type of output of the method and the degree of consistency between this output and the types of information needed for regulatory applications. The output consists of RIRs for NO, AHC, and NHC. RIRs can also be output for anthropogenic area and point sources, as well as for other disaggregations that would be of use. The form of the output, as RIRs, can be directly translated into qualitative control preferences. However, RIRs derived from 12-hour $\text{P}_{\text{O}_3\text{-NO}}^{\text{S}}$ terms may not be appropriate given the present form of the ozone standard, which requires compliance with a one-hour ozone average.

3. Availability of data needed as input to the method. The method requires measurements of NO that are accurate at sub-ppbv concentrations (Cardelino and Chameides, 1995), which appears to exceed the capabilities of most instrumentation that has been, or will be, deployed in routine monitoring networks. The OBM also appears to require continuous gas chromatograph (GC) measurements of hydrocarbon species.

4.4 REFERENCES

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Appendix 4A: DISCUSSION OF NITROGEN-BASED CORRELATION TECHNIQUES

Definitions:

$$\text{NO}_x = \text{NO} + \text{NO}_2$$

$$\text{NO}_y = \text{NO}_x + \text{PAN} + \text{HNO}_3 + \text{ORGANIC-N} \text{ plus } \text{AEROSOL-N}$$

$$\text{NO}_z = \text{NO}_y - \text{NO}_x$$

Many of the observational based analysis methods applied over the last decade have relied on high quality NO_x and NO_y measurements. Several recent studies, designed to characterize air mass aging and the relationship of in-situ ozone production to NO_x or NO_y in rural environments, have produced strong correlations between ozone and various nitrogen groupings (Trainer et al., 1993; Olszyna et al., 1994). These correlations (e.g., Figure 1) generally are based on large quantities of averaged data covering multiple days, and limited to the mid afternoon time period (1 - 5 pm), to filter out the overwhelming negative impact of fresh NO_x titration of ozone. For the same reasons, NO_z - O_3 regressions typically correlate better than NO_y . Ozone should correlate positively with NO_z under NO_x and VOC-limiting conditions, since the radical processes associated with VOC reactions during VOC-limiting conditions coincidentally produce ozone and oxidized nitrogen (NO_z) products such as nitric acid. Collectively, the various studies as well as independent analysis of photochemical model results (Sillman, 1996) suggest that the slope of the regression line can be used as a qualitative indicator for delimiting NO_x and VOC limiting regimes. Progressively higher slopes, $\Delta\text{O}_3/\Delta\text{NO}_z$, reflect NO_x limited regimes and lower slopes reflect a move towards VOC limiting conditions. The existing studies do not provide sufficient guidance to delineate clearly the range of slopes depicting NO_x or VOC limiting regimes, although slopes greater than 8 appear to suggest NO_x -limiting conditions. By themselves, the NO_z - O_3 correlation does not provide a reliable NO_x -VOC-limiting indicator. However, in combination with other observational approaches and photochemical models, the correlation can provide corroborative support for evaluating control effectiveness. Future applications with emerging data bases and cross analysis-method comparisons should provide greater understanding of the utility of these correlation methods.

In addition to providing insight on control strategy effectiveness, the interpretation of NO_x , NO_y and NO_z data can be interpreted to provide insights into air mass aging, ozone production efficiency, and other analyses. Air mass aging can be defined in many ways, but empirical indicators using NO_y and NO_z data are founded on basic, well-understood atmospheric chemistry principles. In simple terms, aging is reflected in observations by the relative amount of NO_x that is oxidized (aged) to various NO_x oxidation products (i.e., NO_z). The ratio, NO/NO_y , is one indicator of air mass aging, and typically is normalized on a range from 0 to 1, with .6 used as a suggested indicator of "photochemically aged" air (Trainer et al., 1993):

$$\text{AGE} = 1 - (\text{NO}_x/\text{NO}_y)$$

Ozone production decreases with aged air masses, and the NO_x -limited conditions almost always associate with aged air masses. Aging analyses can provide guidance as to when to expect good $\text{NO}_z/\text{NO}_y/\text{O}_3$ correlations; poor correlations should be expected with “fresh” air masses. In turn, one might expect “good” correlations between VOC (or selected groups, species) and ozone during periods which are not NO_x -limited, and poor (or coincidentally good) correlations during NO_x -limited conditions. Again, the sum value of the collective use of several analysis techniques across multiple species is greater than the sum of individual analyses.

Data limitations/Relation to PAMS. PAMS will result in an enormous expansion of the VOC data base, and significant, but inadequate, improvements in nitrogen measurements. PAMS introduces additional spatial and temporal coverage of traditional NO_x measurements. However, many of the NO_x instruments are not capable measuring sub-ppb levels. More troubling is the lack of true NO_2 or NO_y measurements. Many of the PAMS NO_x instruments overestimate NO_2 (and therefore NO_x as well), due to PAN and nitric acid interferences. This interference is stronger during daytime conditions, further compromising the utility of nitrogen-based data analysis techniques. NO_y measurements are not required in the PAMS program. Finally, the majority of currently operating PAMS sites (mostly Type II) reflect urbanized conditions with relatively fresh air masses. One would expect these locations to produce poor correlations and infer VOC limiting conditions.

Model simulation derived methods

Various indicator techniques, which utilize absolute values of selected species or species ratio values, have been developed by analyzing photochemical model simulations. These include NO_y (Milford et al., 1994; Sillman, 1995) along with nitric acid, HNO_3 , hydrogen peroxide, H_2O_2 and formaldehyde, HCHO. Results from two different photochemical models suggested that ozone would be limited by VOC at ambient NO_y levels exceeding a threshold level ranging from 10 to 25 ppb, and NO_x controls would not result in increased ozone unless ambient NO_y levels exceeded 20-30 ppb (Milford et al., 1994). Sillman (1995) reported similar results for NO_y , but concluded that the ratios, $\text{HCHO}/\text{NO}_y < 0.28$ and $\text{H}_2\text{O}_2/\text{NO}_y < 0.4$ were effective indicators for VOC limited regimes.

Relation to PAMS. Although these studies are based on model simulations, they provide direction toward the types of measurements useful for inferring control strategy directions. The potential value of NO_y measurements is reinforced by these studies. As discussed above, NO_y measurements are not required by PAMS but are considered an incremental improvement that gradually could be incorporated in the program. In combination with HCHO, which is measured in PAMS, another possible corroborative indicator, HCHO/NO_y , could be available. Hydrogen peroxide is still considered a “research” level measurement. However, peroxide concentrations gradually are becoming standard components of field campaigns such as the SOS. In addition to an indicator application described here, peroxide measurement are extremely useful for model diagnosis and evaluation and should be given strong consideration as a PAMS species when and if monitoring technology allows for more routine H_2O_2 measurements.

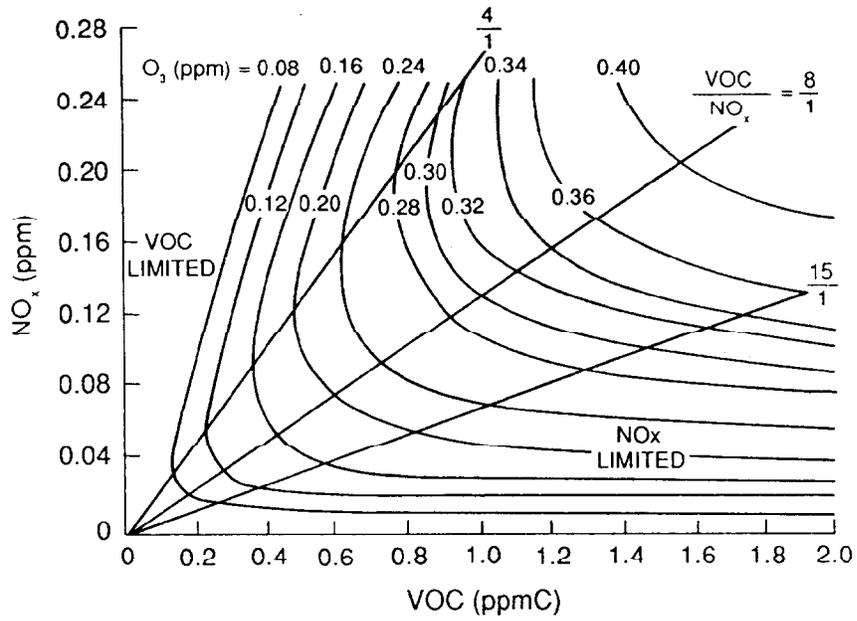


Figure 4-1. Isopleths developed from EPA's EKMA to illustrate VOC/NO_x ratios. (NRC, 1991).

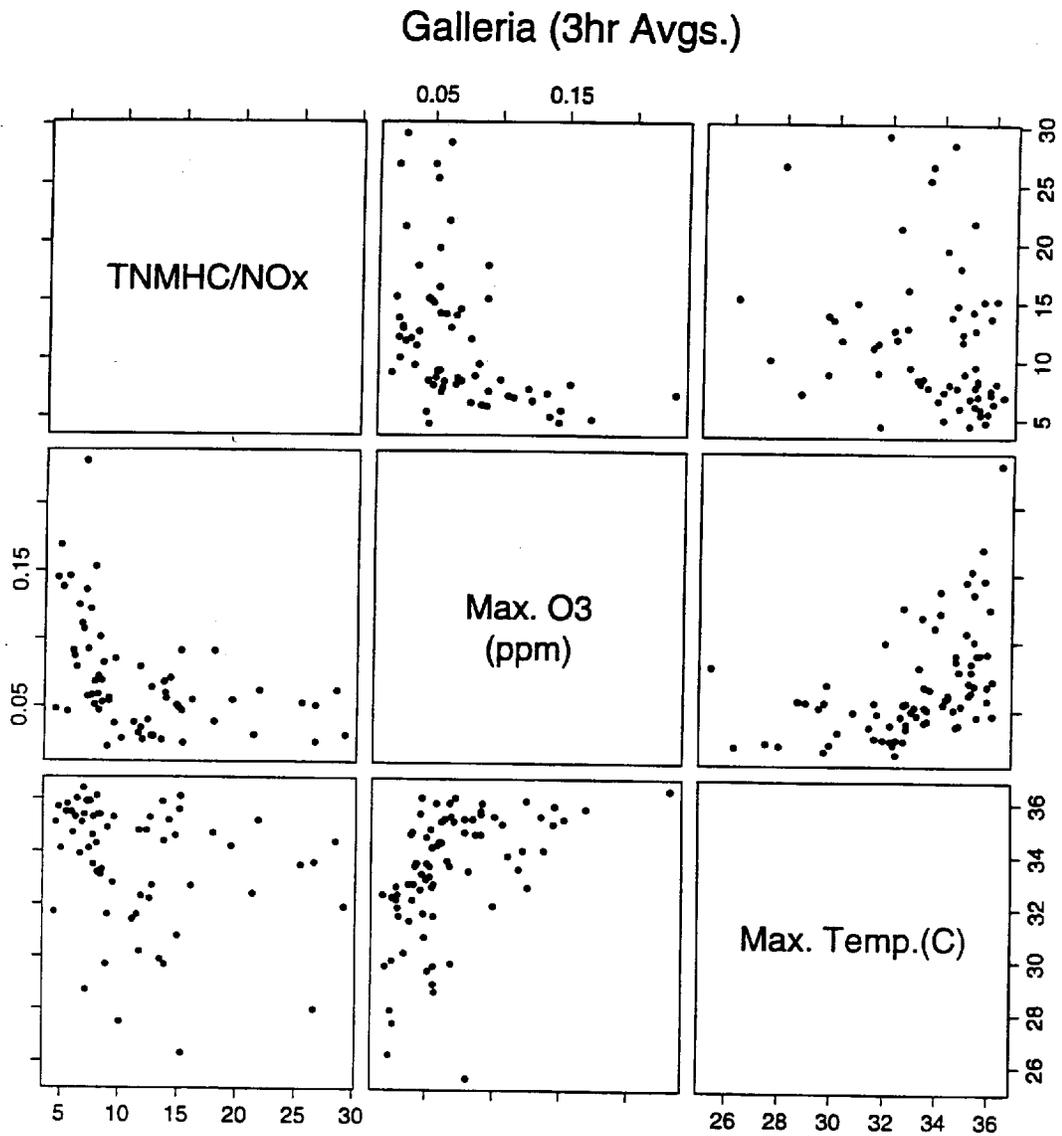


Figure 4-2. Scatter plot matrix for 6-9 a.m. TNMHC/NO_x ratio, daily maximum temperature at Galleria, TX site and regional daily maximum ozone

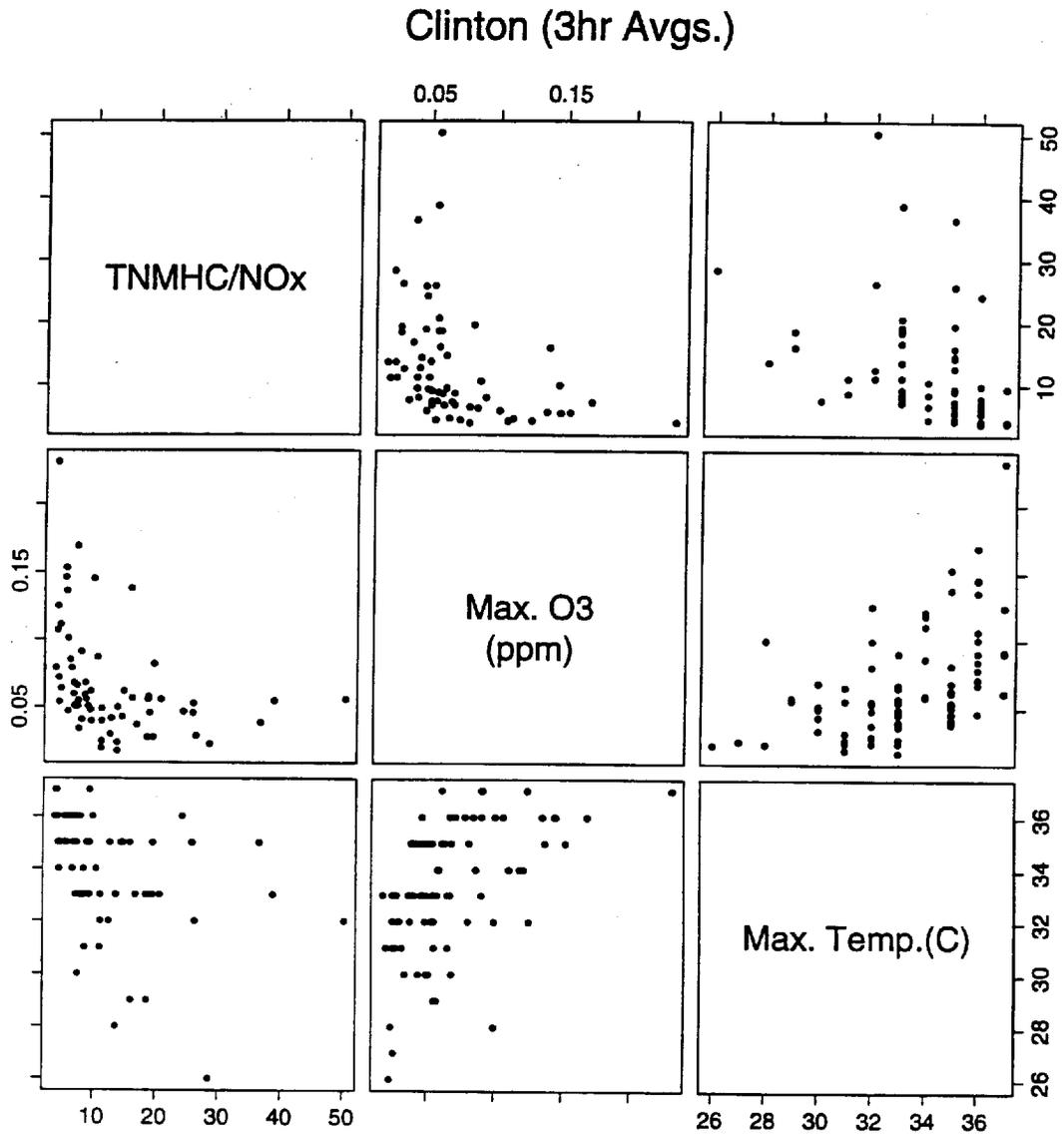


Figure 4-3. Scatter plot matrix for 6-9 a.m. TNMHC/NO_x ratio, daily maximum temperature at Clinton Drive, TX site and regional daily maximum ozone

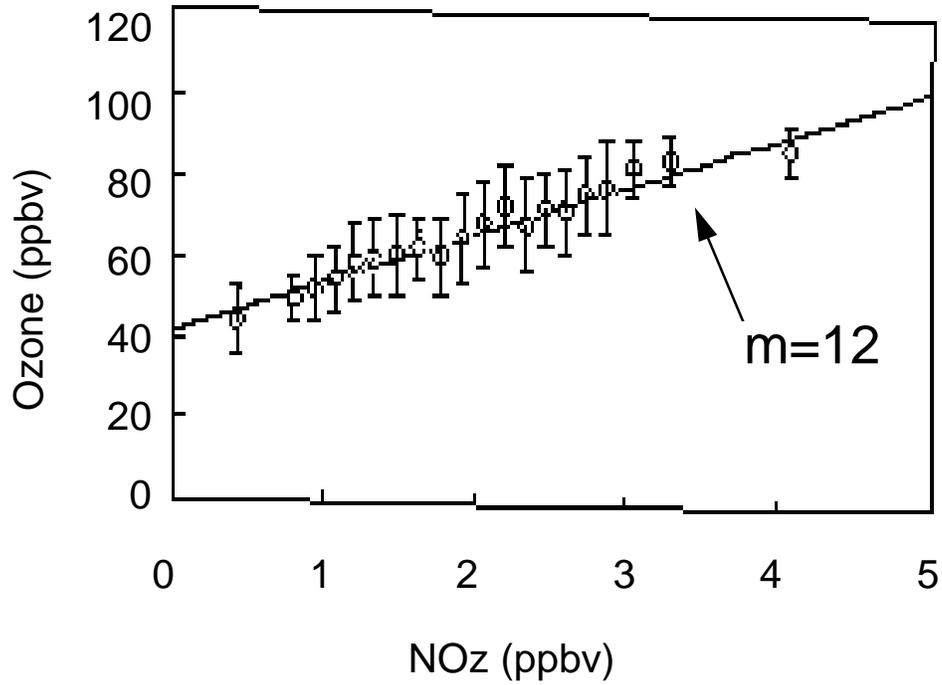


Figure 4-4. Plot of ozone versus NOz for Giles County, TN (Olszyna et al., 1994).

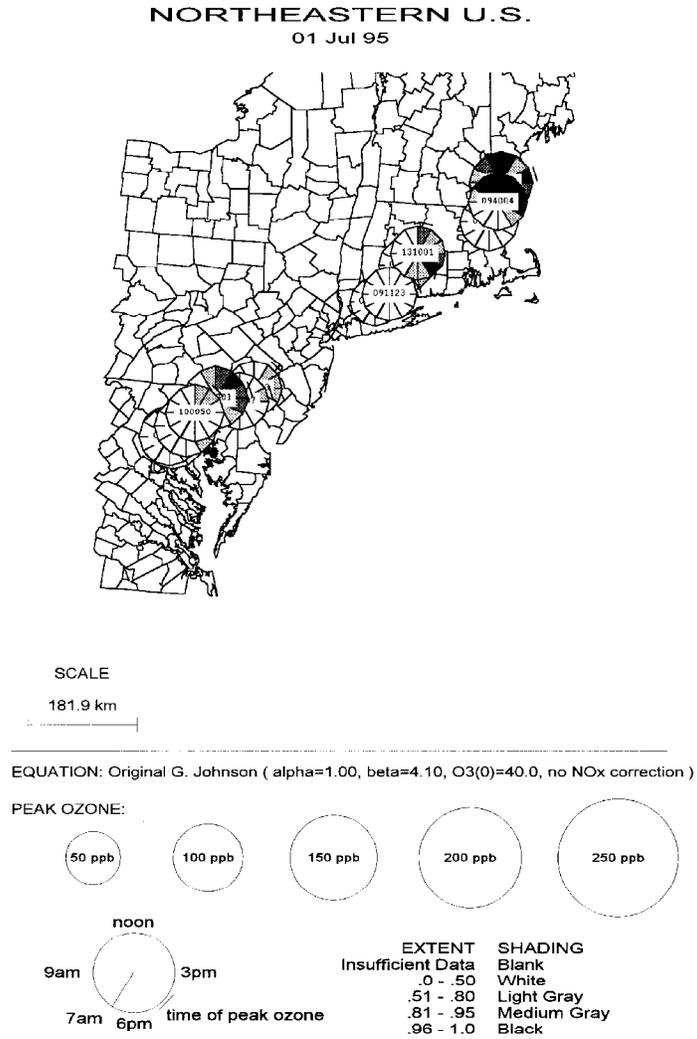


Figure 4-5. Example MAPPER output for the Northeast U.S.

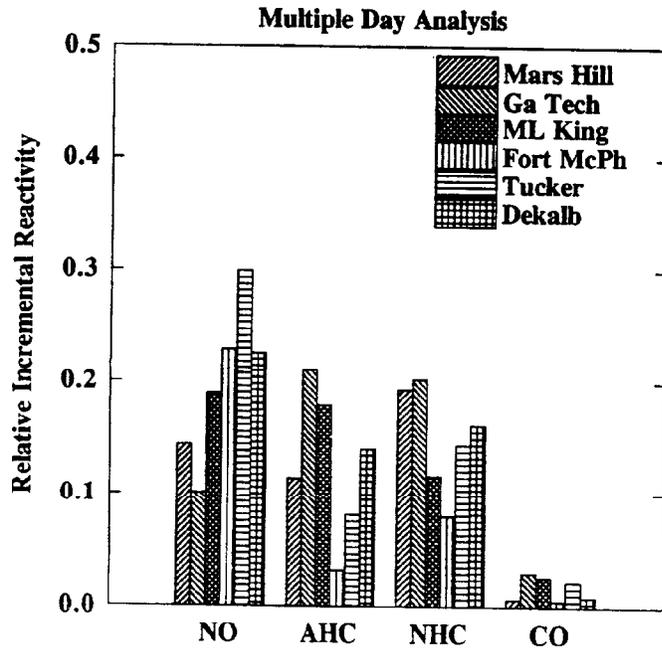


Figure 4-6. Results from GIT-OBM applied to Atlanta. The model provides a relative assessment of the role of emissions groups on ozone formation. (Cardelino and Chameides, 1995).

TABLE 4-1. Summary statistics for TNMHC/NO_x ratios calculated from 3-hour average TNMHC and NO_x concentrations.

	Min.	1st Qu.	Median	Mean	3rd Qu.	Max.	S.D.	NA's	N
All 3-Hour Values									
Galleria	4.457	9.531	13.72	16.94	19.99	94.25	11.165	218	736
Clinton	3.857	11.2	19.22	22.76	29.86	141.2	15.648	297	736
Capitol	2.475	6.927	9.562	12.19	14.48	82.6	9.536	181	739
6-9 a.m. Averages									
Galleria	4.457	7.367	9.524	11.78	14.4	29.22	6.166	28	92
Clinton	3.857	6.751	9.522	12.91	16.47	50.26	9.187	29	92
Capitol	3.738	7.558	10.2	12.51	14.66	45.28	7.798	22	92