REVISIONS TO THE STATE IMPLEMENTATION PLAN
FOR THE CONTROL OF OZONE AIR POLLUTION

ATTAINMENT DEMONSTRATION FOR THE
HOUSTON/GALVESTON
OZONE NONATTAINMENT AREA

Appendix F

Application of Smog Production Algorithms to the Coastal Oxidant Assessment for Southeast Texas (COAST) Data

TEXAS NATURAL RESOURCE CONSERVATION COMMISSION
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Sonoma Technology, Inc.

APPLICATION OF SMOG PRODUCTION (SP) ALGORITHMS TO THE COASTAL OXIDANT ASSESSMENT FOR SOUTHEAST TEXAS (COAST) DATA

FINAL REPORT
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1. INTRODUCTION

1.1 BACKGROUND

Recently increased attention has been devoted to the use of ambient aerometric data as a means to estimate whether reductions in VOC or NO_x emissions would be more effective in reducing ambient ozone concentrations in specific areas. While grid-based photochemical air quality simulation models (PAQSMs) are recognized as the best available tools for development of ozone control strategies, the accuracy of PAQSMs is limited, supporting data (for input and for diagnostic evaluations) are sparse or lacking for most regions, the time required to obtain suitable data and properly apply the models can be substantial, and the costs of applying these models usefully and effectively can be high. In some areas, reliable applications of photochemical models may not be feasible due to limitations of data or modeling resources. In addition, gridded photochemical model applications made with routine data, rather than with databases obtained from special field studies, may be suspect due to the lack of corroborative data or diagnostic analyses.

Recent studies suggest that analysis of ambient data for the extent of atmospheric chemical reaction may offer an independent means of developing a qualitative understanding of a particular area's sensitivity to reductions in VOC and NO_x emissions (Blanchard et al., 1993a, 1993b). In particular, the Smog Production (SP) algorithm developed by Graham Johnson and coworkers at the Commonwealth Scientific and Industrial Research Organization (CSIRO) in Sydney, Australia, offers promise and merits investigation (Johnson, 1984; Johnson and Quigley, 1989; Johnson et al., 1990; Johnson and Azzi, 1992). Blanchard et al. (1993a, 1993b), and Blanchard and Roth (1994) evaluate assumptions underlying the SP algorithm, carry out sensitivity analyses, and describe a procedure for generating spatial displays of the extent of reaction. Blanchard et al. (1994) evaluate the accuracy of the algorithm by using data from smog-chamber studies and by carrying out simulation studies. Based upon the results of data analyses and simulations, Blanchard et al. (1994) derive a revised set of algorithms; they then show how ambient monitoring data may be used in the new algorithms to estimate extent of reaction.

From June 15 through November 30, 1993, the Coastal Oxidant Assessment for Southeast Texas (COAST) was sponsored by the Texas Natural Resources Conservation Commission (TNRCC). The COAST study generated a large database with which the SP algorithms could be both applied and further evaluated. Moreover, because applications of the Urban Airshed Model (UAM) will be undertaken using the COAST data, there will be an opportunity to compare modeling results and the results of the SP algorithms with respect to each procedure's predictions of the relative effectiveness of VOC or NO_x control strategies.

1.2 OBJECTIVES AND SCOPE

This work assignment is intended to address several objectives:

- Delineation of the spatial domain of NO_x limitation in the Houston area during the 1993 COAST study and during selected time periods of previous years using the revised SP algorithms

- Provision of context for interpreting results, including determination of statistical distributions of NO_x limitation

- Testing of the representativeness of the COAST study days with respect to ozone episodes occurring in other years, from the standpoint of NO_x limitation

The COAST study has provided a rich database, with which a number of additional objectives might be addressed. To put the present study in perspective, we note that the following objectives should be addressed in companion studies rather than in the present work assignment:

- Comparison of results obtained from application of the SP algorithms using ambient monitoring data to results obtained from the AIRTRAK instrument

- Determination of the representativeness of the days examined from the standpoint of meteorology

- Testing of the accuracy of the SP algorithms

- Identification and reconciliation of disparities between the results obtained from the SP algorithms and from photochemical modeling studies

2. METHODS

The revised versions of the SP algorithms (Blanchard et al., 1994) were applied to the 1993 COAST study data and to routine monitoring data collected in the Houston and Beaumont areas from 1988 through 1994. The SP algorithms are summarized briefly here; additional details are available in Blanchard et al. (1994).

2.1 SUMMARY OF JOHNSON'S SP ALGORITHM

The SP algorithms define and use two quantities: smog produced (SP) and the extent of reaction. Johnson (1984) defines SP as:

$$SP(t) = O_3(t) - O_3(0) + NO(0) - NO(t) \tag{1}$$

where all species are expressed in units of concentration (not mass). In situations in which NO_x enters a system over a period of time, NO(0) is replaced by NO(i), which denotes the concentration corresponding to the sum of NO_x inputs. Here NO_x means NO plus NO_2.

SP is a useful variable because: (1) the time derivative of SP is an indicator of the rate of NO oxidation by peroxy radicals and a robust measure of the time required to reach the NO-NO_2 crossover and the NO_2 and O_3 maxima in environmental chambers (Carter and Lurmann, 1991); (2) the environmental chamber studies carried out at the CSIRO in Sydney, Australia indicate that SP displays a linear relationship to cumulative light flux, provided sufficient NO_x is present to sustain ozone production; and (3) since ozone and NO react rapidly and reversibly, their concentrations are not independent (the definition of SP accounts for this dependence).

From the CSIRO environmental-chamber studies, Johnson (1984) reports an empirical relationship between the maximum potential SP (SP_{max}) and NO_x inputs:

$$SP_{max} = \beta * [NO_x(i)] \tag{2}$$

where the value of the parameter ß obtained from the CSIRO experiments was 4.1 ± 0.4. ß is an estimate of the maximum amount of SP potentially produced (SP_{max}) per unit NO_x input.

The extent of reaction (E) was defined by Johnson (1984) as the ratio of the instantaneous smog production to the maximum smog production, i.e.,

$$E(t) = \frac{SP(t)}{SP_{max}} \tag{3}$$

When the extent of reaction reaches one in Johnson's model, smog production ceases because virtually all of the NO_x has reacted. Subsequent photochemical formation of ozone is negligible because the system has consumed all of the NO_x and, therefore, can no longer produce ozone. Situations in which extent reaches one correspond to cases in which peak ozone concentrations could be lowered by reducing NO_x inputs to the system. Regions where the calculated extent of reaction is predominantly less than one during the periods of high ozone concentrations are classified as VOC (or light) limited, indicating that peak ozone concentrations could be lowered by reducing VOC inputs to the system. At locations close to sources of NO_x emissions, extent of reaction would generally be less than one, even in regions where NO_x-limiting conditions are found further downwind.

2.2 THE REVISED SP ALGORITHMS

Blanchard et al. (1994) (1) tested the formulation of the SP algorithms against data from environmental chamber experiments carried out at the University of North Carolina (UNC), the Statewide Air Pollution Research Center (SAPRC) at the University of California at Riverside, and the CSIRO; (2) tested the SP algorithms using a photochemical box model (OZIPR) with two chemical mechanisms; and (3) developed a reformulation of the algorithms that is consistent with both the environmental-chamber data and the chemical mechanisms.

The following terms are defined below for clarity:

F	=	fraction of NO_x emitted as NO
NO_x	=	$NO + NO_2$
NO_y	=	sum of oxidized nitrogen species, i.e., NO_x + PAN + HNO_3 + aerosol nitrate + ...
NO_z	=	$NO_y - NO_x$
A	=	A(t), concentration of species A at time t, i.e., where convenient and unambiguous, suppress "(t)"
A(0)	=	concentration of species A at time t = 0
DA(t)	=	concentration of species A at time t corresponding to the mass lost to deposition from time zero to t.

For convenience, all measurements are expressed in units of concentration. Note that assumed values of deposition velocity and mixing heights are used to calculate the deposition term. Details of procedures for calculating various parameters are provided in Blanchard et al. (1994).

Blanchard et al. (1994) re-defined SP as:

$$SP(t) = O_3(t) + DO_3(t) - O_3(0) + NO(i) - NO(t) \tag{4}$$

where they added the term $DO_3(t)$ to the definition of SP to account for the cumulative ozone lost to deposition from time zero to t (i.e., ozone that has been produced but lost to deposition).

Blanchard et al. (1994) found that both environmental-chamber data and simulations carried out using a photochemical box model (OZIPR) (Gery and Crouse, 1992) with the Carbon Bond 4 Mechanism (CBM-4) (Gery et al., 1989) and the Carter-Atkinson-Lurmann-Lloyd (CALL) mechanism (Lurmann et al., 1987) indicated that the maximum potential SP that could be produced in an environmental chamber (or an air parcel) was:

$$SP_{max} = \beta [NO_x(i)]^{\alpha} \tag{5}$$

where α=0.7, β=2 (when measurements are expressed in ppm), and $NO_x(i)$ is the initial concentration of NO_x (i.e., NO + NO_2). SP_{max} was independent of VOC concentrations.

The environmental-chamber data and simulations also indicated that SP(t) could be expressed in the same functional form as SP_{max}, i.e.:

$$SP(t) = \beta [NO_x(i) - NO_x(t)]^{\alpha} \tag{6}$$

Consequently, extent of reaction can be determined by dividing either Equation 4 or 6 by Equation 5:

$$E(t) = \frac{SP(t)}{SP_{max}} = \frac{O_3(t) + DO_3(t) - O_3(0) + NO(i) - NO(t)}{\beta * [NO_x(i)]^{\alpha}} \tag{7}$$

$$E(t) = \frac{SP(t)}{SP_{max}} = [1 - \frac{NO_x(t)}{NO_x(i)}]^{\alpha} \tag{8}$$

In both Equations 7 and 8, an estimate is needed for the initial NO_x. Blanchard et al. (1994) provide two alternative expressions for $NO_x(i)$, the first which is:

$$NO_x(i) = NO_y(t) + DNO_y(t) \tag{9}$$

where $NO_x(i)$ refers to the (hypothetical) concentration at time t corresponding to the mass of NO_x input into the system from time zero to time t (it does not refer to the concentration of NO_x occurring in the undiluted air mass at time zero). Equation 9 expresses the requirement of mass balance for NO_y. This equation requires values for NO_y and estimation of the deposition of NO_y. Thus, this expression is strictly applicable only when true NO_y measurements are available.

The second alternative expression for $NO_x(i)$ is:

$$NO_x(i) = NO_x(t) + W^{1/\alpha} \tag{10}$$

where W is defined as $\{NO_x(i) - NO_x(t)\}^{\alpha}$; W is obtained as the solution of the following equation:

$$\beta * W - F * W^{1/\alpha} = O_3(t) + DO_3(t) - O_3(0) + F * NO_x(t) - NO(t) \tag{11}$$

Equation 11 requires a numeric solution; however, exact solutions can be obtained in the special cases α = ⅓, ½, ⅔, and 1 (Blanchard et al., 1994). Blanchard et al. (1994) recommend using α = ⅔, in which case Equation 10 becomes:

$$NO_x(i) = NO_x(t) + [\frac{\beta}{3F}]^3 * [2X+1]^3 \tag{12}$$

where:

$$X = \cos[\frac{4\pi + \cos^{-1}(C)}{3}]$$

$$C = 1 - \frac{27(\gamma/F)}{2(\beta/F)^3} \quad for\ -1 \le C \le 1$$

$$\gamma = O_3(t) + DO_3(t) - O_3(0) + F * NO_x(t) - NO(t)$$

The full derivation of the revised equations may be found in Blanchard et al. (1994).

2.3 APPLICATION OF THE SP ALGORITHMS TO TEXAS DATA

Calculations were carried out for all monitoring sites having both ozone and "NO_x"[1] data (see **Table 2-1**). Both COAST and AIRS data were used. The COAST and AIRS data at Aldine and Clinton did not always yield identical extents of reaction because the NO_x values in the two databases were not identical (however, the differences in NO_x concentration were generally 0 to 3 ppb). For several other sites, the O_3 and NO_x data from the COAST and AIRS databases were often significantly different. We do not know the reasons for these differences.

The calculations were carried out several ways to bound the extent of reaction. Because only standard chemiluminescent "NO_x" measurements were available, the measured concentrations overestimate the concentrations of true NO_x ($NO + NO_2$) and underestimate the concentrations of true NO_y (the sum of all oxidized nitrogen species). The effects of these measurement biases are to underestimate the extent of reaction when using the NO_x version of the SP algorithm and to overestimate extent when using the NO_y version.

The calculations all use 40 ppb background ozone, $O_3(0)$. The extents of reaction for the COAST data were calculated using (1) the NO_y version of the revised SP algorithm, (2) the NO_x version of the revised algorithm, and (3) the NO_x version of the revised algorithm with an assumed diurnal profile of PAN subtracted from the measured NO_x concentrations (the assumed profile peaks at 2 p.m. at 2 ppb PAN). The Houston and Beaumont results (1988 through 1994 routine data) were calculated using the NO_y version of the revised SP algorithm because the "NO_x" data prior to 1993 are reported only to the nearest 10 ppb (in the NO_x version of the algorithms, extent of reaction approaches one only as NO_x concentrations fall to a few ppb or less; in the NO_y version, extent approaches one as NO_y falls to about 8 to 15 ppb).

All summary statistics were computed using the NO_y version of the revised algorithm. **Table 2-2** shows the parameter values used for the calculations.

2.4 LIMITATIONS

The SP algorithms are based on the analysis of environmental-chamber data and simulations carried out using a box model. These systems all have fixed volumes and an initial charge of NO_x and VOCs. Because the algorithms are not yet fully developed for systems subject to dilution and continuous injection of emissions, the application of the algorithms to ambient data is potentially subject to biases that have not yet been determined. A second study, which is now in progress, will investigate the importance of these biases on this report's results by examining other air quality and meteorological data.

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[1] The term "NO_x" is used here to denote measurements of NO_x that include not only NO and NO_2 but also unquantified interferences from species such as PAN and HNO_3.

Table 2-1. Monitoring sites used in the analyses.

Code	Name	Latitude	Longitude	Database
BMTC	Beaumont C02	94.0668	30.0392	COAST
C35C	Clinton CGC/Harris	95.2578	29.7336	COAST
CRSC	Crosby AQ/Met Site	95.0731	29.9511	COAST
GALC	Galveston AQ Site	94.8564	29.2631	COAST
GILC	Gilchrist	94.4600	29.5200	COAST
GLRC	Galleria CGC Site	95.4628	29.7222	COAST
H01H	HRM Site 1	95.2556	29.7144	COAST
H03H	HRM Site 3	95.1814	29.7653	COAST
H04H	HRM Site 4	95.1319	29.8347	COAST
H07H	HRM Site 7	95.0175	29.7689	COAST
H08H	HRM Site 8	95.0564	29.6461	COAST
H10H	HRM Site 10	94.9214	29.8789	COAST
H11H	HRM Site 11	94.9103	29.7658	COAST
HALC	Aldine C8/Harris Co.	95.3264	29.9011	COAST
HCFA	Site T-19 Crawford	95.3614	29.7519	COAST
HLAA	Site T-26 Lang	95.4956	29.8350	COAST
HTCC	Texas Commerce Tower	95.3636	29.7603	COAST
S40S	SETRPC Site 40 (Sabine Pass)	93.8969	29.7181	COAST
S41S	SETRPC Site 41 (West Orange)	93.7689	30.0750	COAST
S42S	SETRPC Site 42 (Mauriceville)	93.8731	30.1800	COAST
S43S	SETRPC Site 43 (Jefferson Co. Airport)	94.0039	29.9369	COAST
SBRC	Seabrook C20	95.0172	29.5722	COAST
SPTC	Smith Point AQ/Met	94.7578	29.5342	COAST
STWC	Stowell (Winnie) AQ/Met	94.4067	29.7928	COAST
WORA	West Orange C9	93.7617	30.0858	COAST
ALDN	4510 Aldine	95.3258	29.8750	AIRS
LANG	4401 Lang Road	95.4956	29.8350	AIRS
MAE	1262 Mae Drive	95.2222	29.7714	AIRS
CLIN	9525 Clinton Drive	95.2569	29.7333	AIRS
CRAW	Crawford at Polk	95.3614	29.7519	AIRS
SABN	Sabine Pass	93.8969	29.7181	AIRS
WORA	West Orange	93.7689	30.0750	AIRS
MAUR	Mauriceville	93.8731	30.1800	AIRS
BAIR	Jefferson Co. Airport	94.0039	29.9369	AIRS

Table 2-2. Parameter values used in calculating the extent of reaction.

Parameter		Value
Equation	Revised:	NO_x and NO_y versions (maps)
		NO_y version only (statistical summaries)
Alpha (α		⅔
Beta (ß)		19.00
F		0.95
$O_3(0)$		40.0 ppb
Min $V_d(O_3)$		0.20 cm sec^{-1}
Max $V_d(O_3)$		0.50 cm sec^{-1}
Min $V_d(NO_y)$		0.20 cm sec^{-1}
Max $V_d(NO_y)$		0.50 cm sec^{-1}
Z(0600)		200 m
Zmax		1500 m
Z(1800)		1200 m
time(Zmax)		15.00 hours
time(Zdec)		16.00 hours

3. RESULTS

Map displays of the extent of reaction are shown in Appendix A for each COAST intensive day on which exceedances of the ozone standard occurred. **Figure 3-1** shows an example display for August 19, when the highest ozone concentration occurred (231 ppb at Aldine). In the maps, each circle represents a 12-hr clock, beginning at 7 a.m. and ending at 6 p.m. (the hours are located as on a conventional clock face). The radius of each clock is proportional to the daily peak ozone concentration, as shown in the legend of each figure. The times at which the peak ozone occurred are denoted by the line outside the perimeter of each clock. The shading indicates the hourly values of extent, as delineated in the legend of each figure. These maps thus show the geographical locations of the highest ozone concentrations and the extent of reaction at the times of the ozone peaks (as well as at other times).

For each date, separate maps show the results obtained with the NO_y, NO_x, and adjusted-NO_x versions of the revised SP algorithm. As described earlier, adjusted-NO_x refers to the use of the NO_x version with an assumed diurnal profile of PAN subtracted from the measured NO_x concentrations (the assumed profile peaks at 2 p.m. at 2 ppb PAN). Because chemiluminescent "NO_x" concentrations were used as if they represented true NO_x and true NO_y concentrations, the map displays underestimate the extent of reaction when using the NO_x version of the SP algorithm and overestimate extent when using the NO_y version. Thus, the NO_x- and NO_y-based maps should be viewed as bounding the actual extent of reaction. The maps that are based on the adjusted NO_x concentrations provide an indication of the sensitivity of the NO_x-based algorithm to biases in the NO_x measurements.

Figures 3-1, 3-2, and 3-3 show the displays for the NO_y, NO_x, and adjusted NO_x versions of the algorithm for August 19. The NO_y version (Figure 3-1) indicates NO_x limitation occurring at Aldine (HALC), Crosby (CRSC), Seabrook (SBRC), Galveston (GALC), HRM Site 10 (H10H), Stowell (STWC), Beaumont (BMTC), SETRPC Site 42 (Mauriceville, S42S), and SETRPC Site 43 (Jefferson County Airport, S43S). The NO_x version (Figure 3-2) indicates NO_x limitation occurring at Aldine and Galveston. Figures 3-1 and 3-2 together bound the actual extent of reaction. Because the NO_x version, which underestimates extent when "NO_x" data are used, indicates that extent reaches one at Aldine and Galveston, there is evidence that these two sites were NO_x limited on August 19. Conversely, because the NO_y version overestimates the extent of reaction when "NO_x" data are used, sites such as Crawford (HCFA), Lang (HLAA), and HRM Site 4 (H04H), at which all hours have extent less than 0.8, show no evidence of NO_x limitation on August 19.

Appendix B shows the percentiles of the distribution of the extent of reaction calculated for each site over the duration of COAST study. As shown in Table B-3, three sites, Beaumont (BMTC), SETRPC Site 41 (West Orange, S41S), and West Orange (WORA) experienced no hours with ozone concentrations exceeding 124 ppb. At all other sites, the median extent of reaction was greater on exceedance days than on other days (compare tables B-1 and B-2).

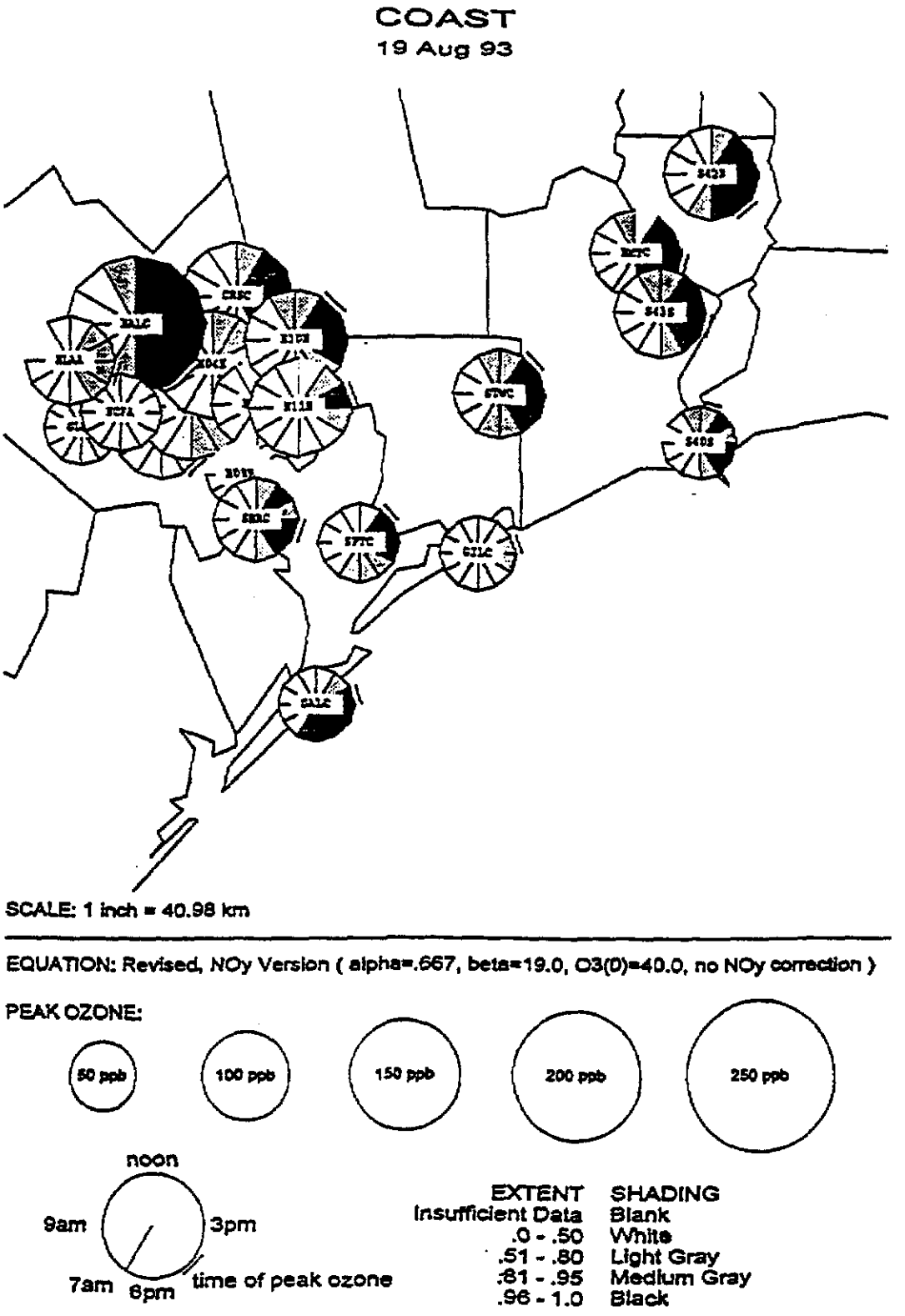

Figure 3-1. Example map display for August 19, 1993, calculated using the NO_y version of the algorithm.

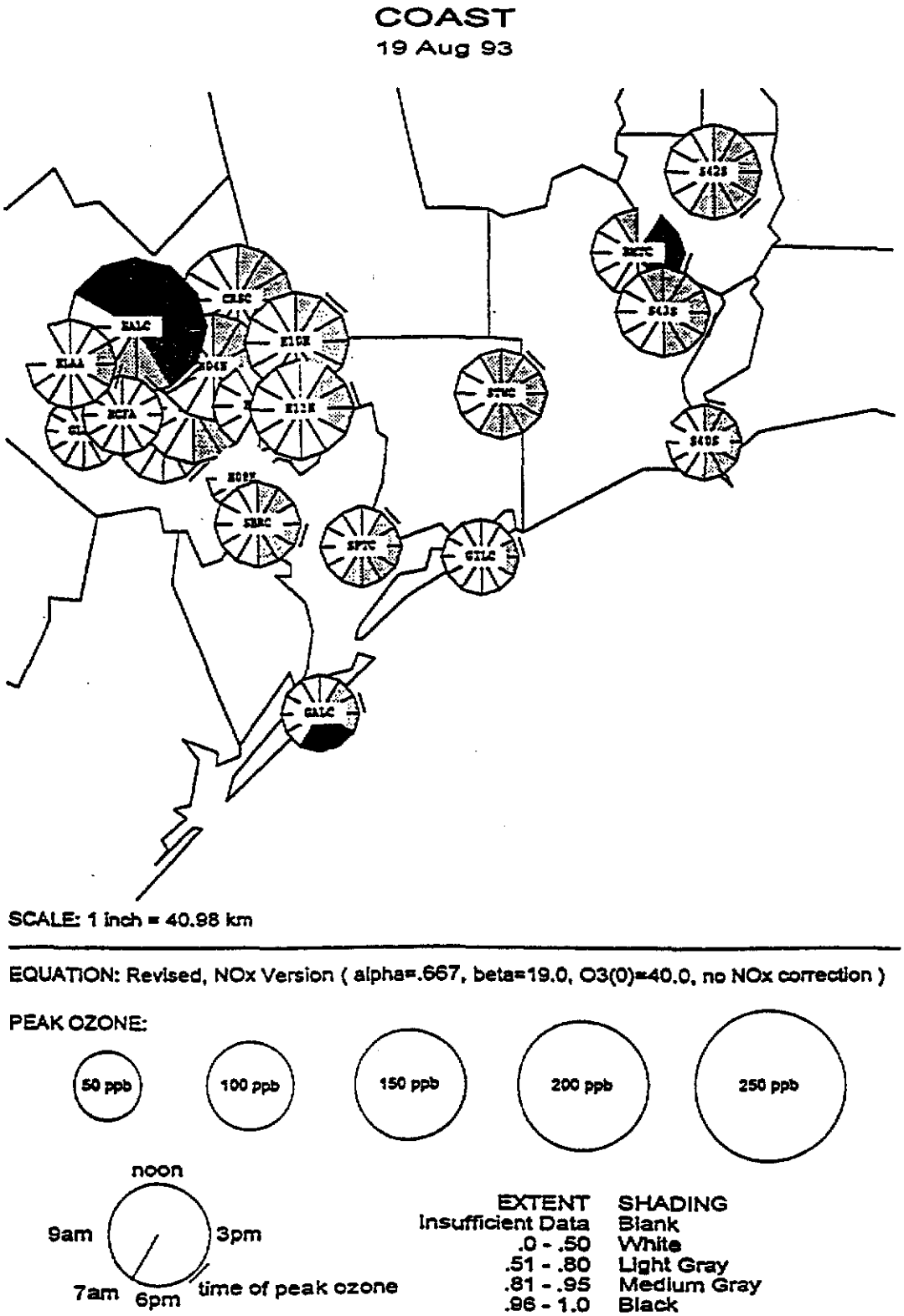

Figure 3-2. Example map display for August 19, 1993, calculated using the NO_x version of the algorithm.

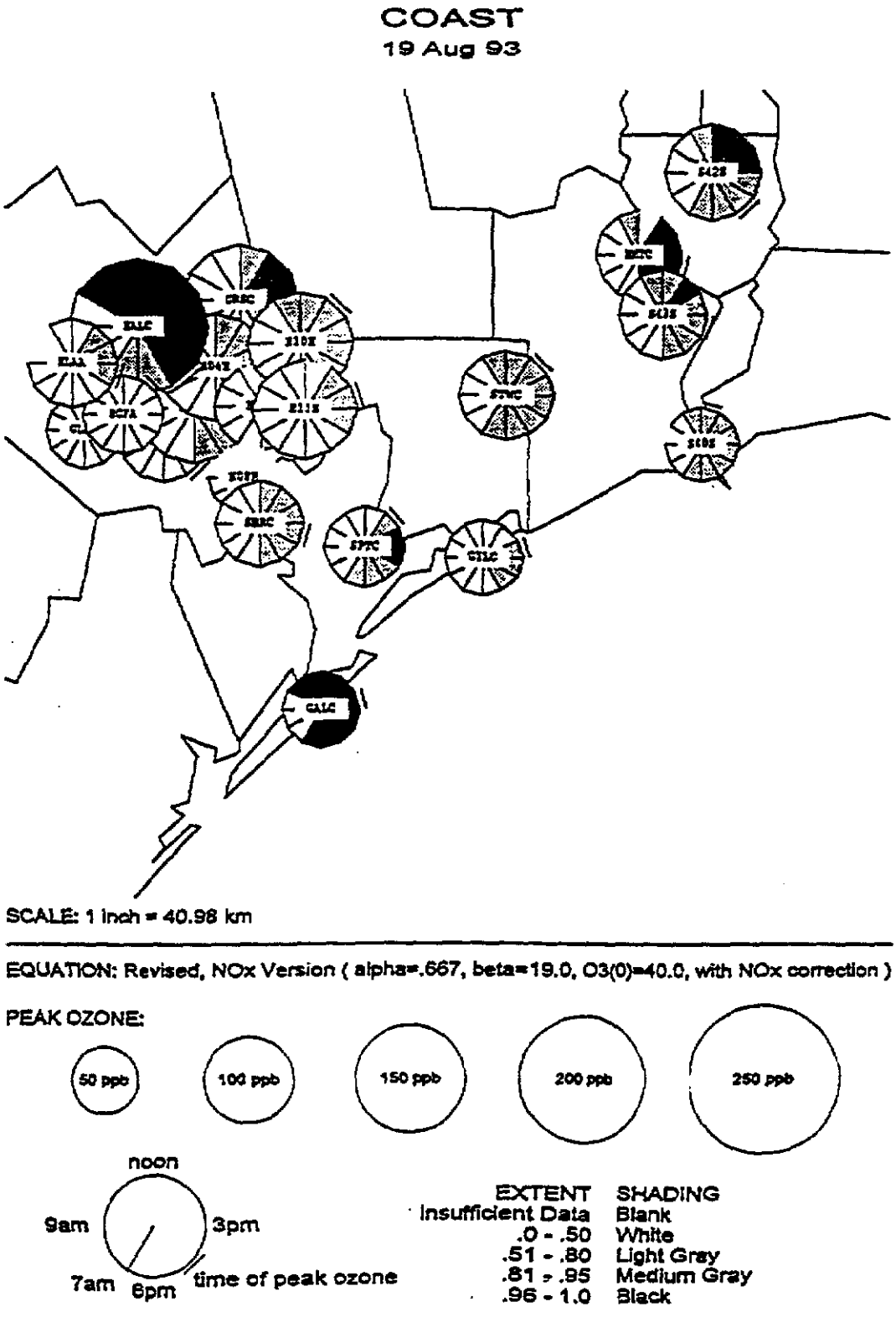

Figure 3-3. Example map display for August 19, 1993, calculated using the adjusted NO_x version of the algorithm.

Because extent of reaction was computed using "NO_x" data with the NO_y version of the algorithm, values obtained for extent are overestimated during times when the "NO_x" measurements did not include all components of NO_y (e.g., during hours of peak ozone concentrations, HNO_3 concentrations could have been a few ppb, which may not have been included in the measured "NO_x" concentrations). Since extent may be overestimated during some time periods, it can be concluded that the eight sites at which the extent of reaction was less than one during all exceedance hours showed no evidence of NO_x limitation; these sites are Galleria (GLRC), HRM Site 1 (H01H), HRM Site 3 (H03H), HRM Site 8 (H08H), Crawford (HCFA), Lang (HLAA), Texas Commerce Tower (HTCC), and SETRPC Site 42 (Mauriceville, S42S). As shown in the map displays in Appendix A (e.g., August 19), seven of these eight sites are centrally located in Harris County; the eighth site (Mauriceville) is northeast of Beaumont. Thus, extent of reaction is usually well below one (and NO_x is not limiting) at sites near major emissions sources, as expected.

Four sites, Aldine (HALC), Gilchrist (GILC), SETRPC Site 43 (Jefferson County Airport, S43S), and Stowell (STWC) exhibited an extent of one during all exceedance hours, although the Jefferson County Airport and Stowell sites only had two exceedance hours each. The lower-bound estimate of the extent of reaction for Aldine, which experienced the area's highest ozone concentration on August 19 (231 ppb), was also one for several hours that day. Thus, Aldine, Gilchrist, Jefferson County Airport, and Stowell showed strong evidence of NO_x limitation.

Extent was one for a majority of exceedance hours at four sites: Crosby (CRSC), Galveston (GALC), Sabine Pass (S40S), and Smith Point (SPTC). Air parcels at these sites exhibit NO_x limitations a significant amount of time. At the remaining six sites, Clinton (C35C), HRM Site 4 (H04H), HRM Site 7 (H07H), HRM Site 10 (H10H), HRM Site 11 (H11H), and Seabrook (SBRC), extent ranged from about 0.3 to 1.0 during exceedance hours. These sites thus showed varying degrees of NO_x limitation.

Appendix C shows statistical distributions of the extent of reaction at sites where ozone and "NO_x" concentrations were monitored from 1988 through 1994. Because the "NO_x" data prior to 1993 were rounded to the nearest 10 ppb, the resulting values for the extent of reaction have greater uncertainties than would have been the case had the "NO_x" concentrations been reported to the nearest ppb. However, the data and calculations from the earlier years may be used for comparison with 1993.

Figures 3-4 through 3-8 illustrate the distributions that are shown in Appendix C for five sites: Aldine, Clinton, Crawford, Lang, and Mae. At Aldine, the median extent of reaction during exceedance hours was about 0.9 to 1.0 in all years (the tick mark that denotes the median is hidden at the margin of the graph when the median is one). At the other sites, the median extent of reaction was about 0.6 to 0.8 in all years. Neither the range nor the median varied appreciably from year to year.

As shown in greater detail in Appendix C, the statistical distributions of the extent of reaction during exceedances of the ozone standard prior to 1993 did not differ appreciably from those occurring in 1993. Thus, the extent of reaction results for 1993 during COAST are similar to previous years.

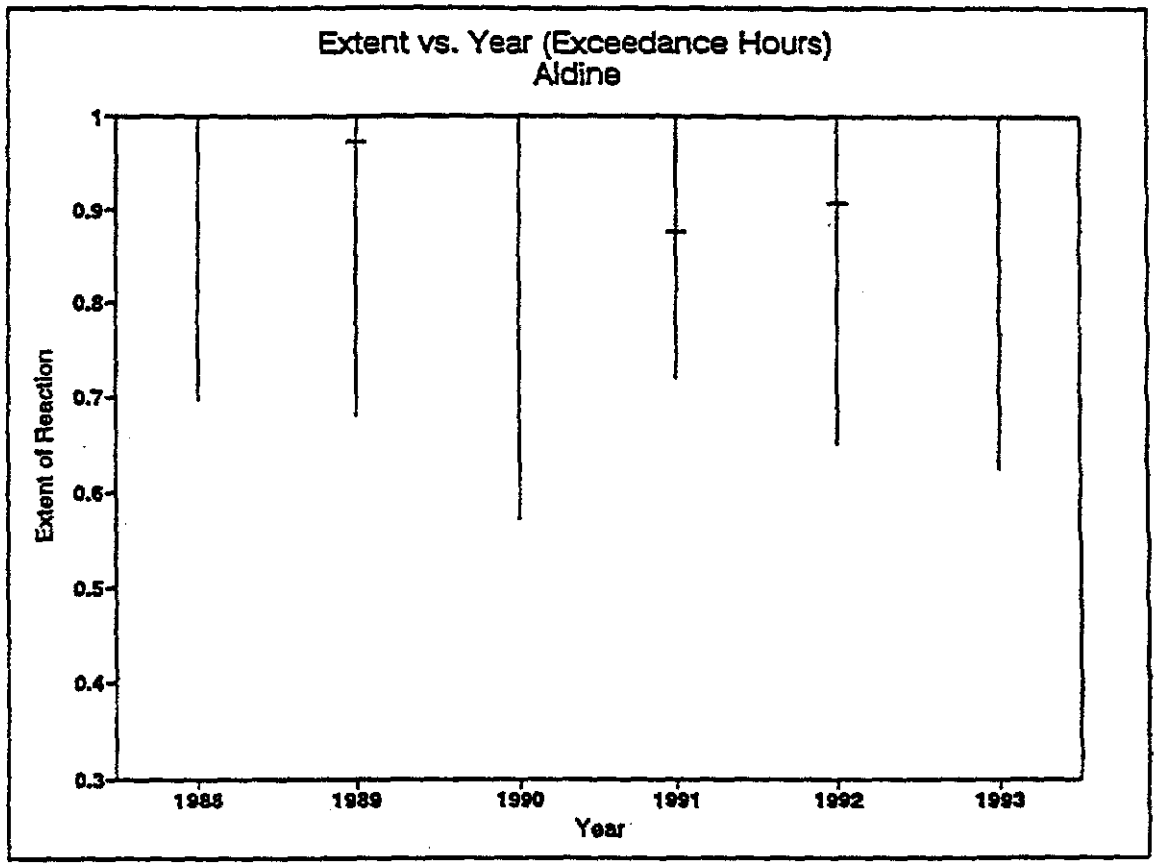

Figure 3-4. Minimum, median, and maximum extent of reaction during exceedance hours versus year at Aldine, using the NO_y version of the revised SP algorithm (the tick mark that denotes the median is hidden at the margin when the median is one).

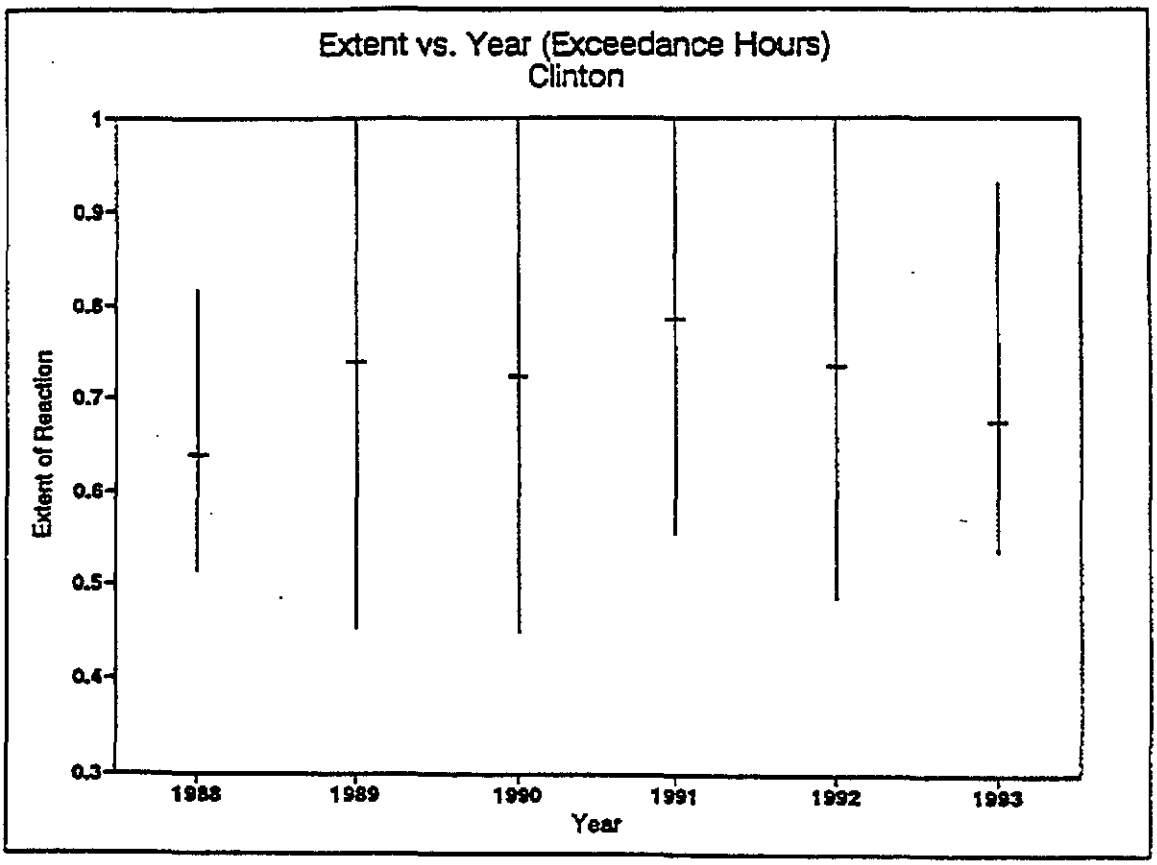

Figure 3-5. Minimum, median, and maximum extent of reaction during exceedance hours versus year at Clinton, using the NO_y version of the revised SP algorithm.

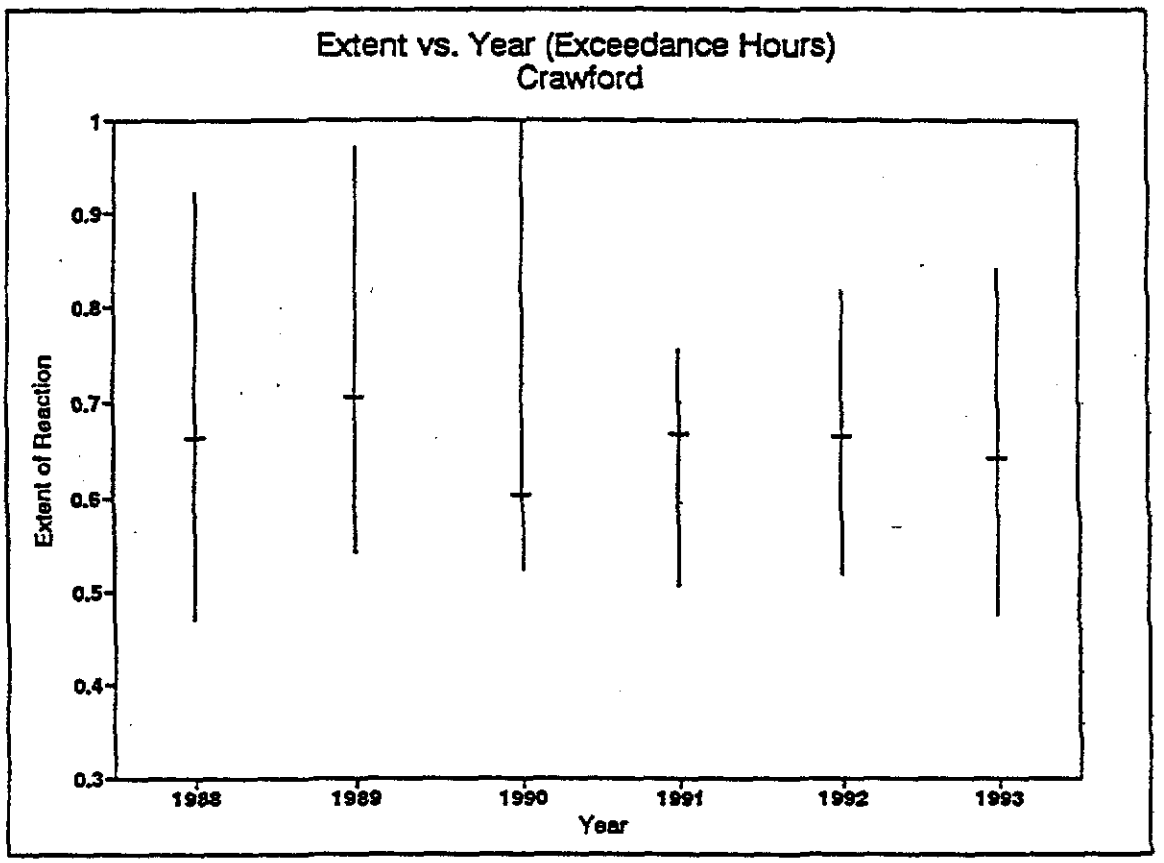

Figure 3-6. Minimum, median, and maximum extent of reaction during exceedance hours versus year at Crawford, using the NO_y version of the revised SP algorithm.

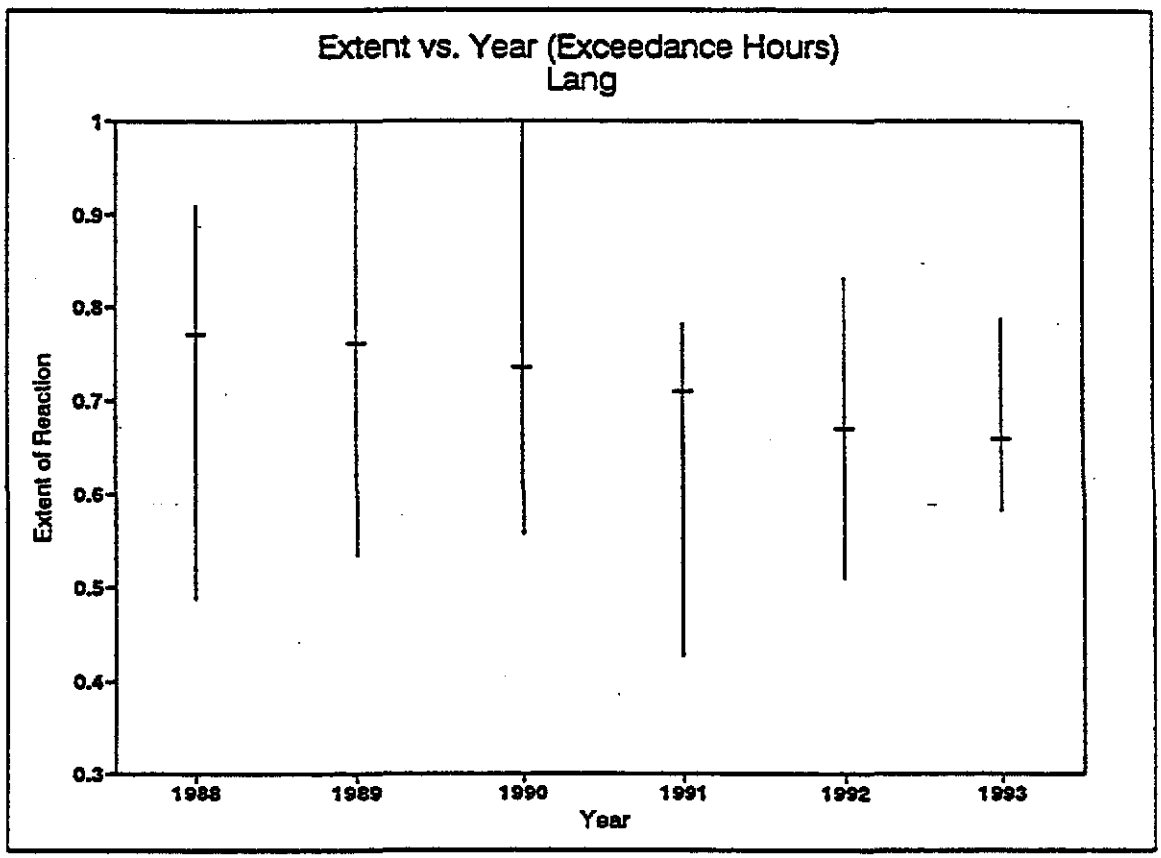

Figure 3-7. Minimum, median, and maximum extent of reaction during exceedance hours versus year at Lang, using the NO_y version of the revised SP algorithm.

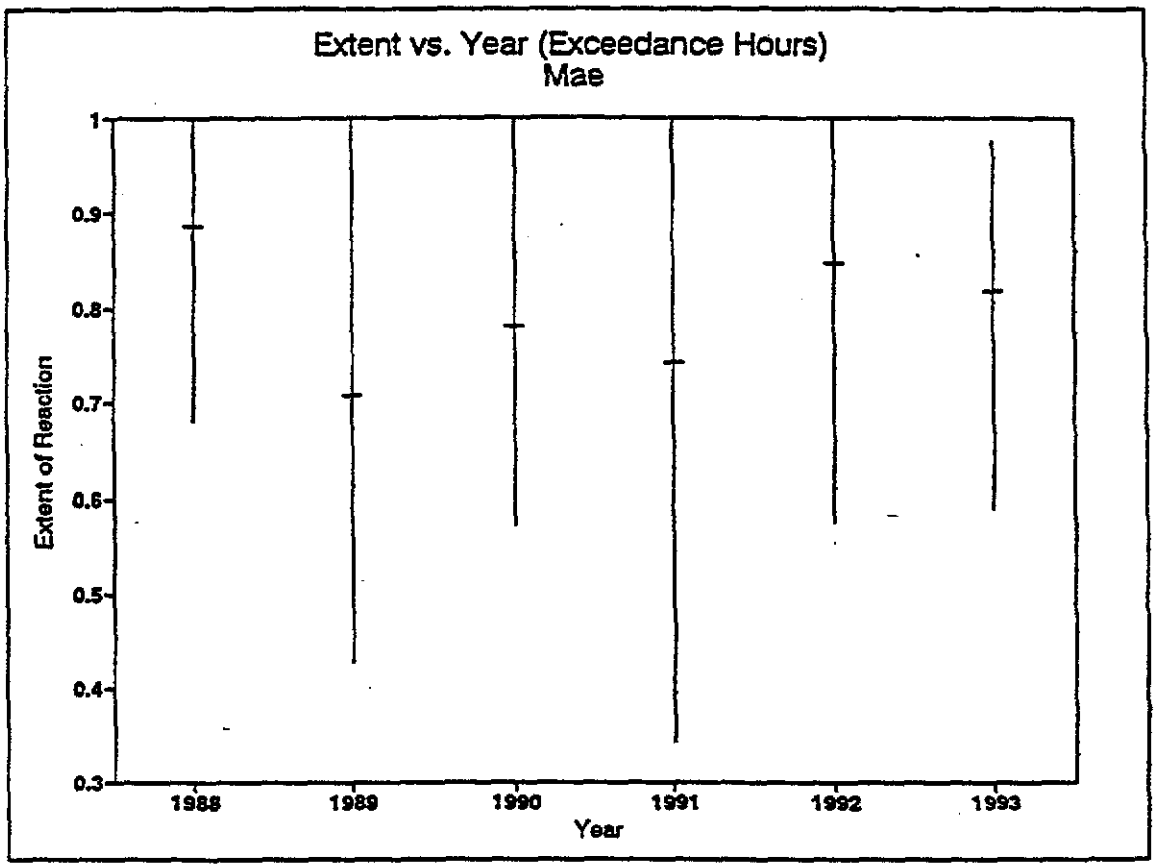

Figure 3-8. Minimum, median, and maximum extent of reaction during exceedance hours versus year at Mae, using the NO_y version of the revised SP algorithm.

4. CONCLUSION AND RECOMMENDATIONS

The revised versions of the SP algorithm (Blanchard et al., 1994) were applied to the 1993 COAST study data and to routine monitoring data collected in the Houston and Beaumont areas from 1988 through 1994. Routine O_3 and "NO_x" data were used in the calculations. The "NO_x" data includes an unknown interference from other oxidized nitrogen species, notably PAN and HNO_3; and thus the "NO_x" concentrations overestimate true NO_x ($NO + NO_2$), but underestimate NO_y. These routine "NO_x" measurements have been used in NO_x and NO_y versions of the SP algorithm, thus providing a lower and upper bound to the true extent of reaction.

The principal conclusions of this study are:

- Three COAST sites, Beaumont (BMTC), SETRPC Site 41 (West Orange, S41S), and West Orange (WORA) experienced no hours with ozone concentrations exceeding 124 ppb. At all other sites, the median extent of reaction was greater on exceedance days than on nonexceedance days.

- During the COAST study, eight sites did not reach an extent of one during exceedances of the ozone standard, thus showing no evidence of NO_x limitation. These sites, Galleria (GLRC), HRM Site 1 (H01H), HRM Site 3 (H03H), HRM Site 8 (H08H), Crawford (HCFA), Lang (HLAA), Texas Commerce Tower (HTCC), and SETRPC Site 42 (Mauriceville, S42S), are centrally located in Harris County, except S42S, which is northeast of Beaumont. Thus, extent of reaction is usually well below one (and NO_x is not limiting) at sites near major emissions sources, as expected.

- Four sites, Aldine (HALC), Gilchrist (GILC), SETRPC Site 43 (Jefferson County Airport, S43S), and Stowell (SWTC), exhibited an extent of one during all exceedance hours, thus strongly indicating NO_x limited conditions. However, there were only two exceedance hours at S43S and Stowell.

- Extent was one for a majority of exceedance hours at four sites; Crosby (CRSC), Galveston (GALC), Sabine Pass (S40S), and Smith Point (SPTC). Air parcels at these sites exhibit NO_x limitations a significant amount of time.

- The remaining six sites exhibited an extent of reaction of one during some exceedance hours.

- There are hours of NO_x limitation within Harris County during exceedances.

- At sites where ozone and "NO_x" concentrations were monitored from 1988 through 1993, the statistical distributions of the extent of reaction during exceedances of the ozone standard prior to 1993 were similar to those occurring in 1993.

The principal recommendations are:

- The results obtained here should be compared with assessments of control preferences derived from other analyses of the ambient monitoring data and from modeling studies, when they become available.

- The findings from such comparisons should be used to improve the SP algorithms, if evidence of inaccuracies in the algorithm arises.

- Further applications of the SP algorithms would benefit from the availability of true NO_x and NO_y data.

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Due to the length, the appendices associated with this report
are not available in electronic file.

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