

3. Observation-based analyses in support of weight-of-evidence arguments

3.1 Airborne canisters sampled during TexAQS 2000

The 2000 Texas Air Quality Study (TexAQS 2000) collected an extensive amount of ambient VOC data in and around the Houston area. Included in this large dataset are hydrocarbon canisters collected on board aircraft. The reactivity of these samples were calculated and the spatial and temporal variations were studied. The entire study is presented in Attachment 5, but the conclusions are presented below.

- High reactivity canisters usually found near industrial areas. Those found outside industrial areas were generally either dominated by biogenic isoprene, or could be linked to industrial emissions by trajectory analysis.
- Reactivity analysis of canisters shows that ethylene and propylene commonly dominate the total reactivity, comprising about 35% of the reactivity on average. Other important compounds include butenes, butanes, isoprene, trimethylbenzenes and alkanes.
- Canisters collected during the modeled ozone episode (August 22 - September 1 2000) usually had their total reactivity dominated by ethylene and propylene, with occasional large contributions by butenes, 1,3-butadiene, toluene, and alkanes. The samples with the highest reactivity were dominated by butenes, propylene, and 1,3-butadiene.
- One sample collected on Aug 30, 2000 seemed to deviate greatly from the composition expected by the reported emissions inventory. A modeling sensitivity analysis was performed using emissions that were adjusted to be consistent with the observed concentrations. The ozone performance of this sensitivity analysis was extremely good in an area that had been very difficult to simulate accurately in previous runs, suggesting that the canister has intercepted a plume of emissions that were not accurately quantified in the inventory.

3.2 Automated gas chromatography data

Two separate studies were performed with automated gas chromatography (auto-gc) data: an analysis of the reactivity of VOCs observed between 1996-2001, and a preliminary study to reconcile the observed light olefin emission signals with the reported emissions inventory.

Reactivity analysis of auto-gc data

Automated gas chromatograph data collected at seven TCEQ monitoring sites (Clinton CAMS 403, Deer Park CAMS 35, Channelview CAMS 15, Aldine, Bayland Park, HRM 3, and HRM 7) were analyzed to answer the following questions:

- Which volatile organic compounds (VOCs) are likely to be most important in ozone formation in Houston?
- Does the atmospheric VOC mixture and reactivity vary geographically in the Houston

- area?
- How often do conditions of high VOC reactivity occur in Houston?

In the original SIP revision proposal of June 2002, twelve compounds and compound groups were listed as candidates for regulation, based upon their reactivities and upon the observations by Brookhaven National Laboratory (BNL) scientists during the TexAQS 2000 study. These twelve compounds and compound groups were ethylene, propylene, all butene isomers, all pentene isomers, 1,3-butadiene, isoprene, all trimethylbenzene isomers, all xylene isomers, toluene, all ethyltoluene isomers, formaldehyde and acetaldehyde. The initial list was developed from the analyses that had been completed at that time. Subsequent analyses, including this analysis, were performed in order to refine the list by using data collected over a longer time period (1996-2001) to assess which compounds contributed most to ozone reactivity.

The second question relates to source attribution. TexAQS 2000 data indicated that the reactivity of the VOC mixture emanating from the industrial areas of Houston was often much higher than the urban VOC mixture. This analysis attempted to verify or refute that finding using the multi-year auto-GC data set, and to determine if there were additional geographic variations that might be useful in source attribution.

The third question is directed toward discovering the roles of “routine emissions” and “upsets” in setting the composition of the VOC mixtures observed in Houston. There is much ambiguity in how “routine emissions” and “upsets” are defined, in that “routine” emissions can apparently be continuous or sporadic, and “upsets” can apparently be brief or prolonged. This analysis bypasses the question of defining these terms, and simply asks how often high reactivity is observed. If high reactivity is observed often, then whatever type of release is causing these conditions is not rare.

Table 3-1. VOC data available from auto-GCs in the Houston area

Site Name	Start date	End date	Number of hours available
Clinton	Aug 20, 1996	Oct 31, 2001	26,868
Deer Park	Jan 16, 1997	Oct 31, 2001	17,547
HRM 7	Aug 27, 2001	Oct 31, 2001	1375
HRM 3	Aug 21, 2001	Oct 31, 2001	1505
Channelview	Aug 4, 2001	Oct 31, 2001	1195
Aldine	Aug 31, 2000	July 30, 2001	3034
Bayland Park	May 4, 1998	Aug 7, 2000	5783

Table 3-1 shows that a very large sample of data were available for this study from two sites, Clinton and Deer Park. At the other sites, data were available mostly for time periods that did not overlap with the canister samples taken during the TexAQS 2000 study. Therefore, the data set in this study represents a much broader time period than the TexAQS 2000 canisters. The auto-GCs were operated according to EPA PAMS site guidelines and TCEQ guidelines. The auto-GC data and meteorological data were validated by TCEQ staff. Additional QA and peer review was performed by Sonoma Technology; more detail is available from Main et al., 2002.

The auto-gc reactivity study is presented in its entirety in Attachment 6, but the conclusions from this study are presented below:

Which VOCs are likely to be most important in ozone formation in Houston?

These compounds were *frequently* responsible for high reactivity days: **propylene, ethylene, butenes** (1-butene, c-2-butene, t-2-butene), and **1,3-butadiene**.

A second group of highly reactive compounds exhibited very high reactivity *occasionally*: pentenes, xylenes, and hexenes.

A third group of compounds, n-butane and isobutane, are normally low reactivity compounds, but have been detected in such extremely high concentrations that they are responsible for very high reactivity.

Several compounds identified earlier as candidates for regulation have not been detected at high reactivities during summertime midday conditions by the auto-GCs: toluene, ethyltoluenes, and trimethylbenzenes. However, toluene and trimethylbenzenes caused high reactivity in several TexAQS 2000 airborne canister samples. Styrene, which was considered for the list of candidate compounds, has not been seen at high reactivities in midday summer samples.

Many compounds that may contribute to high reactivity are not measured by the auto-GCs. Two compounds that are known to play an important role in ozone formation, formaldehyde and acetaldehyde, are not measured by the auto-GCs, but are measured using other techniques routinely by TCEQ. These carbonyl data will be analyzed later. Additional analyses of BNL, NOAA, NCAR, Baylor/EPA, event-triggered canisters, HRM network canisters, TCEQ toxics monitoring, and other data sets may reveal other compounds that play a large role in reactivity.

Does the atmospheric VOC mixture and reactivity vary geographically in the Houston area?

Auto-GCs have sampled at seven locations in Houston, and the composition of the VOC mixture observed at these different sites varies substantially. At most sites, ethylene and propylene are the dominant contributors to reactivity, but the secondary contributors vary from site to site. Composition of the VOC mixture at Bayland Park and Aldine, the two sites influenced most by urban emissions rather than industrial emissions, have very similar compositions. Composition at the industrial sites of Channelview, Clinton, Deer Park, HRM 3 and HRM 7, however, vary substantially, probably due to the type of industries in the vicinity of the monitoring sites. Additional monitoring data at many different sites in the industrial area are essential to determining the overall variability of VOC mixture so that all compounds responsible for high reactivity can be identified.

How often do conditions of high VOC reactivity occur in Houston?

At three auto-GC sites in close proximity to industry, high reactivity occurs 50-60% of the time; at two others, high reactivity occurs 30-40% of the time. At two auto-GC sites well removed

from the industrial complex, high reactivity occurs less than 10% of the time. The frequent occurrence of high reactivity suggests that regardless of whether emission events are defined as “routine” or “upsets”, they seem to occur more than half the time in the industrial areas

Preliminary emission adjustment factors for C2-C4 olefins using automated gas chromatography data

Another analysis was performed on the auto-gc data to answer the following questions:

1. Are the observed light olefin concentrations consistent with the reported emissions inventory?
2. How much the emissions inventory should be adjusted within different regions in the Houston area?

Each auto-gc site observes high concentrations of light olefins when the wind blows from some directions but not others (Figure 3-1). This analysis utilizes these clear emission signals that appear in selected wind directions to estimate whether the reported inventory is approximately correct or not. Specifically, the observed ratio of light olefin concentration to NO_x concentration was compared to the same ratio reported in the emissions inventory, for selected wind directions. If the observed ratio is greater than the reported ratio, the emissions are assumed to be under-reported.

This preliminary analysis is based upon many assumptions, some of which have not been examined completely. For example, the reported point source NO_x emissions are assumed to be correct, which is a good assumption if the NO_x has been quantified using continuous emissions monitoring of a stack, but not a good assumption if a less reliable method has been used. Another assumption is that the light olefin and NO_x emissions from a group of point sources is well mixed, so that the observed ratio is representative of all emissions within the group. These assumptions and other potential sources of bias are discussed more fully in Attachment 7.

The preliminary emission adjustments are presented in Table 3-2. Different adjustments were calculated for different parts of the Houston area, because the auto-gc data seemed to indicate that some source clusters had greater discrepancies than others in their reported olefin emissions.

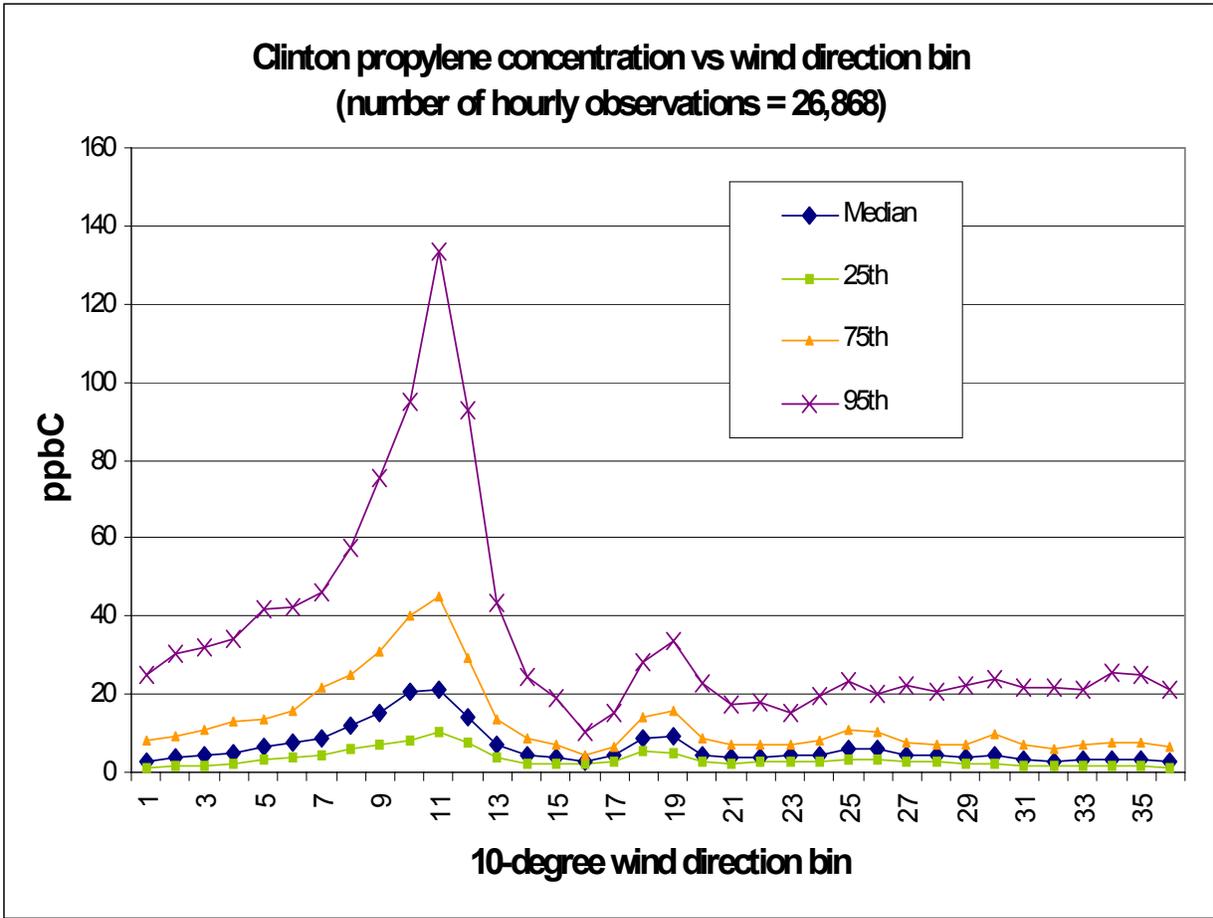


Figure 3-1. Propylene concentrations as a function of wind direction at Clinton auto-gc. The site clearly sees a distinct signal from the areas with reported propylene emissions.

Table 3-2. Reported and inferred C2-C4 olefin emissions for source clusters, using auto-GC data.

Source Cluster	Reported emissions (tons/day)	Inferred emissions (tons/day)
West Ship Channel 2	1.48	3.13
West Ship Channel 1	1.22	1.51
West Central Ship Channel	1.21	2.78
East Central Ship Channel	0.66	5.00
East Ship Channel	8.10	47.5
Baytown	2.81	39.5
Channelview	3.16	5.95
Mont Belvieu	1.75	3.88
Bayport	0.92	11.9

These emission adjustments were used in a CAMx sensitivity run, but have not been used in the base case upon which the SIP revision is based. However, the emission adjustments used in the base case are very similar to those calculated here. Also note that in this analysis, emission adjustments have only been calculated for light olefins, but there are good indications that similar adjustments will be needed for many other VOCs as well.

3.3 Observational Modeling of Houston Air Performed by Weinheimer and Flocke at the National Center for Atmospheric Research (NCAR), Boulder

Observation-based modeling was performed by scientists from the National Center for Atmospheric Research, and is presented here as further evidence of the effectiveness of olefin control strategies.

The results below are derived from a complex observational model simulation that is set up to replicate the chemical composition in actual air samples taken in the Houston Ship Channel area during the TexAQS 2000. The “box” modeling uses the NCAR Master Mechanism (Madronich), a complex chemical mechanism that explicitly includes 800 chemical species and 2200 reactions. The condensed mechanisms usually used in photochemical grid modeling generally model only a few species explicitly, and the rest are represented by lumped species that approximate the behavior of a class of compounds. The strength of the observational model is that it used actual chemical composition observed in the air over the Ship Channel area and uses a sophisticated chemical mechanism to simulate atmospheric reactions.

A limitation of these results is that this observational model does not account for transport, dilution, deposition, or injection of additional fresh emissions into the air as it moves down wind. In addition, this model simulates the reactions occurring in an average, well-mixed, partially-

aged air parcel downwind of the industrial areas, not a fresh plume. The behavior of a fresh plume of olefins or NO_x may be quite different from what these observational model scenarios depict. The results from the box modeling are in agreement with the sensitivities conducted by the TCEQ and increases the confidence that the findings are directionally correct.

Use of the Observational Model Simulation

VOC concentrations were averaged from 23 canisters collected over the entire field study representing Ship Channel air in which light olefins were contributing to rapid ozone formation. NO_x concentrations were averaged in the same manner, that is, over the same time periods over which the 23 canister samples were collected.

Sensitivity Runs

TCEQ staff requested several sensitivity runs to assess the response of air in the Ship Channel area to reductions in NO_x and industrial olefin concentrations. The sensitivity runs performed for the TCEQ included using initial conditions to match observed VOCs during the time of the study.

The typical, U.S. urban VOC composition, which is dominated by mobile source emissions, was derived using data from 39 U.S. cities. Acetylene, a relatively stable compound that is much more resistant to reactions in urban air than ethylene and propene and is not lost through deposition, was used as an indicator of the concentration of mobile source exhaust. The NCAR scientists used the ratios of each measured VOC to acetylene to estimate how much of each VOC observed in Houston came from mobile sources. They assumed that any excess came from industrial emissions.

Figure 3-2 lists the initial conditions for the observation-based modeling and a listing of the typical VOC ratios for U.S. cities. Acetylene is listed using the formal chemical name, “ethyne.” Note that the primary difference between the Houston case and the 39-cities case is the propene concentration, which is nearly four times greater in Houston than in other cities. Also note that VOCs associated with mobile source pollution (e.g., n-pentane, i-pentane) in ground level samples taken in typical U.S. cities are more concentrated than in the air aloft downwind of the Houston industrial areas.

Mixing ratios used for base model runs

	Houston Ship Ch. Obs. x1.0	39 US Cities mix	Hou. Ship Ch. red. alkenes	Hou. Ship Ch. red. alkanes
Ethyne	1.77	6.45	1.77	1.77
Ethane	8.6	11.7	8.6	3.2
Propane	7.7	7.8	7.7	2.2
n-Butane	2.7	10.1	2.7	2.8
i-Butane*	5.0	3.7	5.0	1.0
n-Pentane	1.8	4.4	1.8	1.2
i-Pentane	3.0	9.1	3.0	2.5
Ethene	10.3	10.7	2.9	10.3
Propene	9.5	2.6	0.71	9.5
2-Butene	0.38	0.63	0.17	0.38
1-Butene	1.3	0.74	0.2	1.3
O3	90	90	90	90
PAN	1.9	1.9	1.9	1.9
PPN	0.26	0.26	0.26	0.26
PiBN	0.055	0.055	0.055	0.055
HNO3	5	5	5	5
Acetaldehyde	1.5	1.5	1.5	1.5
Propionaldehyde	0.2	0.2	0.2	0.2

$\text{NO}_x = 20$ ppbv for all

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Figure 3-2: From Weinheimer and Flocke (2002)

To determine the model's sensitivity to reductions in NO_x and olefin concentrations, a series of sensitivity runs were carried out with the observational model. NO_x concentrations were reduced from the ambient levels by 10%, 20%, etc. through 90% and also by 95%. For each level of NO_x , the alkene (olefin) concentration was reduced from ambient levels in three steps down to alkene concentrations observed in an average of samples collected in 39 U.S. cities. The 39-cities concentrations represent approximately the alkene concentrations that would be expected in Houston without the large industrial component. Figure 3-3 shows the results of these simulations.

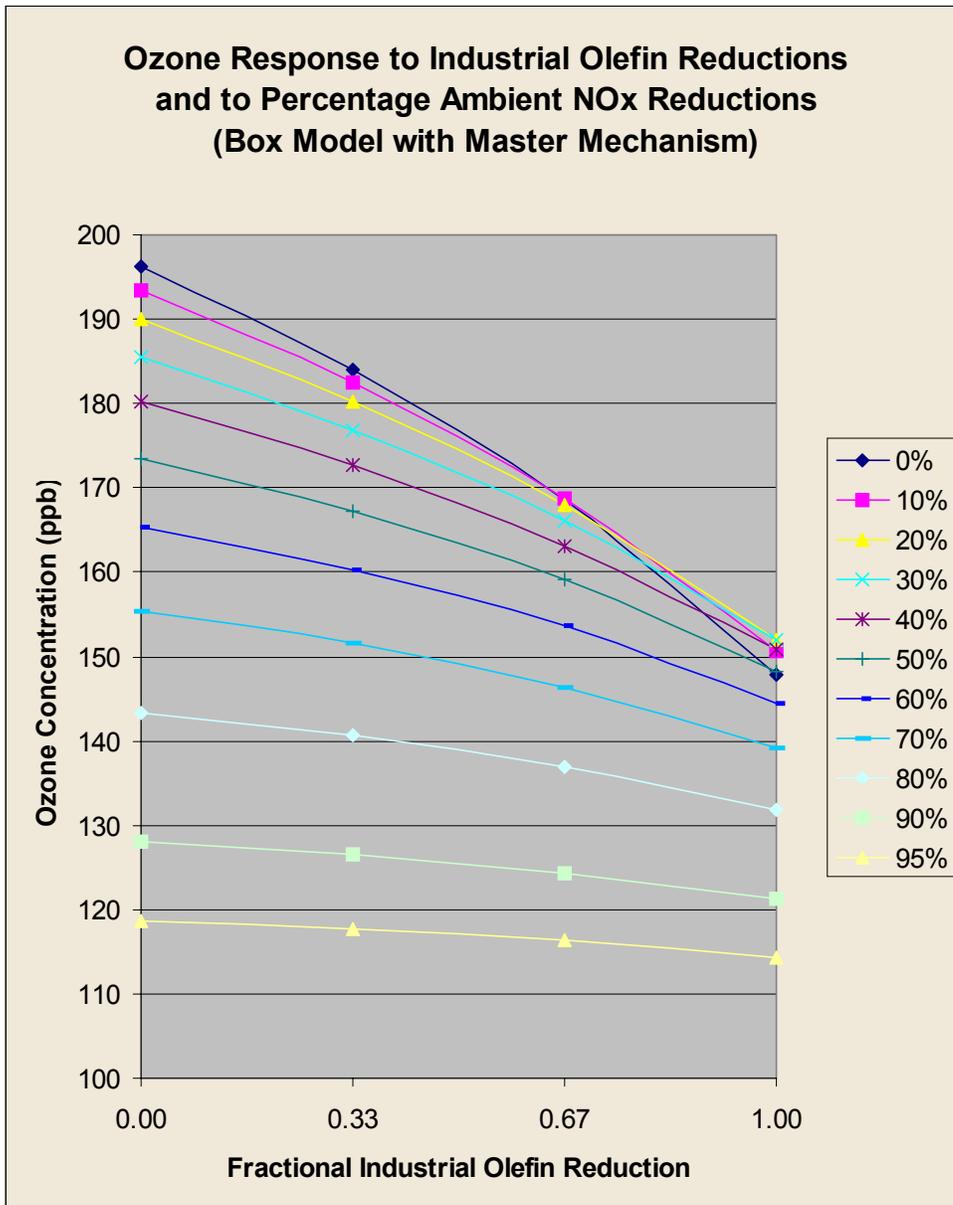


Figure 3-3: Ozone response to Olefin & NO_x reductions (data from Weinheimer & Flocke)

The sensitivity runs gave the ozone response to olefin and NO_x reductions and also provided a comparison of ambient VOC concentrations in Houston to olefin observations in 39 cities where studies have been conducted. It is interesting to note that the observational model indicates that Houston's observed ozone concentrations are about 50 ppb higher than they would be if Houston did not have industrial olefins but instead had olefin concentrations from only nonindustrial sources like those in the 39 cities composite.

Houston's acetylene to carbon monoxide (CO) ratio is higher than observed in other cities. This

finding may result in some of the industrial acetylene emissions' being assigned to mobile source exhaust. If this is the case, the analysis that estimates the nonindustrial contribution to light olefins may have over estimated the contribution of nonindustrial light olefin emissions. Therefore, the actual impact of a percentage reduction in industrial light olefin emissions would be a greater decrease in ozone than is projected in these results.

The results of the observational model were used to determine the amount of olefin reduction that might be necessary to compensate for the last 10% of NO_x reductions as follows: the 2000 modeling inventory described in the next section of this document shows 851 tons/day of NO_x emissions. The 2007 controlled emissions case shows 416 tons/day of NO_x. The future control case (similar to the control case reported in the December 6, 2000 SIP revision) then represents a 51% reduction from the 2000 base inventory. Similarly, a 2007 control case with a nominal 80% reduction in point source NO_x emissions (as opposed to 90% in the 2000 SIP revision) has 519 tons/day of NO_x, which is a reduction of 39% from the 2000 base case. These reductions were interpolated from the original model results, and are plotted in Figure 3-4. The horizontal line represents the target (predicted ozone concentration at the nominal 90% NO_x reduction of the 2000 SIP revision), and the intersection of the 39% NO_x reduction curve with the target line gives the required reduction in industrial olefins that may be necessary to provide ozone reductions equal to those in the original 2000 SIP. This pattern can be found by further interpolation to equal 35%, i.e. reducing industrial olefin emissions by 35% gives the same air quality benefit as the last 10% (80% to 90%) of industrial NO_x emission reductions. The line for 45% NO_x reduction on the graph corresponds to a nominal 85% reduction in point source NO_x emissions, and this curve intersects the target at 20%, so a 20% reduction in industrial olefin emissions could provide equivalent ozone benefits to the last 5% (85% to 90%) of NO_x reductions.

A second photochemical modeling study is in progress at the University of Texas in Austin. Dr. David Allen and colleagues have carried out a different type of modeling, which is described in greater detail in the Accelerated Science Evaluation of Ozone Formation in the Houston-Galveston Area: Atmospheric Chemistry document, located on the web at http://www.tnrc.state.tx.us/air/aqp/airquality_techreports.html#section7. UT's efforts to date have been focused on ozone formation from upset emissions of different hydrocarbons. The UT modeling is directionally consistent with the NCAR Master Mechanism modeling, though they found that the amount of hydrocarbon reduction that might be needed to provide ozone benefits equivalent to 90% NO_x reduction depends greatly on which hydrocarbons are reduced.

It should be noted that this analysis was based on the reductions actually modeled in the December 6, 2000 SIP revision, which had modeled ozone concentrations above the NAAQS. A shortfall, or "gap", calculation was used to determine the amount of additional NO_x reductions that would be necessary to reach attainment, and some additional "gap" rules were adopted in the SIP revision that were not modeled. Referring back to Figure 3-3, there is an indication that as more NO_x is removed from the model, the response to olefin reductions diminishes (the curves "flatten out" towards the bottom of the graph).

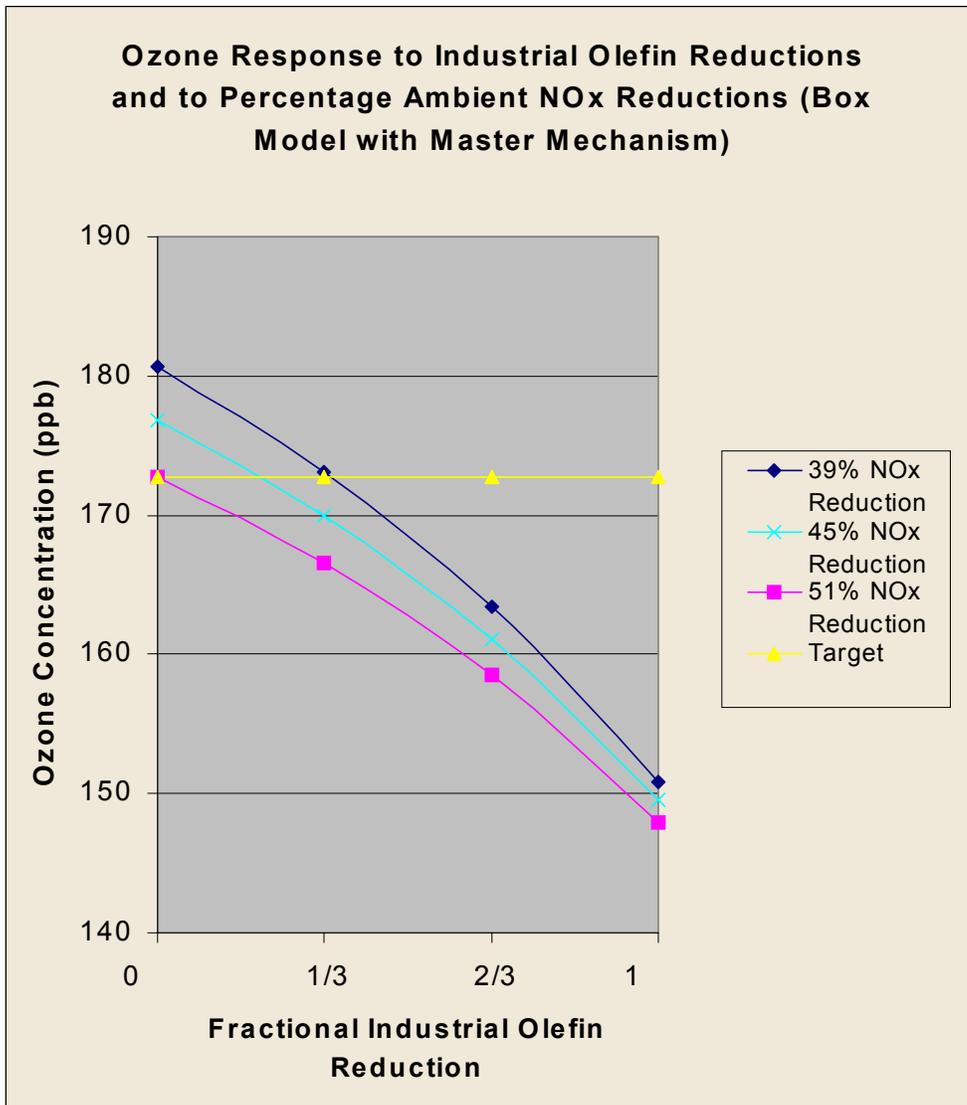


Figure 3-4: Calculation of required olefin reductions to provide equivalent air quality benefits to last 5% and 10% of NO_x reductions