3 Hypotheses of Causes of the Ozone Weekend Effect

3.1 Synopsis

Ozone formation in the atmosphere is complex, and this complexity is in part responsible for the many hypotheses outlined below to explain the weekend effect. Both oxides of nitrogen (NO_X) and volatile organic compounds (VOCs) are necessary to form more than about 0.04 ppm of ozone in the troposphere. An interesting aspect of the ozone chemistry is that ozone formation will peak at an optimum VOC and NO_X mixture, usually where the VOC concentrations about 6 to 9 times higher than the NO_X concentrations (or at a VOC to NO_X ratio of 6 to 9). At conditions where the VOC to NO_X ratio is greater than 6 to 9, the amount of NO_X limits the amount of ozone formed, and ozone formation is characterized as NO_X-limited. At conditions where the ratio is less than 6 to 9 the VOCs limit the amount of ozone formed and ozone formation is characterized as VOC-limited. In both situations, reducing the limiting precursor will reduce the amount of ozone formed. However, not as obvious, is that increasing the levels of the non-limiting precursor will also reduce the amount of ozone formed because its increased levels will enhance reactions that limit ozone production. Because of this effect, it is possible to reduce the non-limiting precursor's concentration and still form more ozone. This phenomenon is the basis of the first hypothesis discussed below.

Four hypotheses to explain the increased ozone concentrations on the weekend are explained below. Each hypothesis is offered as a scientific proposition. Much of the available data has been reviewed by ARB staff and has been compared to the hypotheses to determine which hypothesis or hypotheses provide a consistent explanation of the data and the results of these analyses are discussed later in this report. Each hypothesis is explained below.

1) VOC-Limited (NO_X-Disbenefit, NO_X-Reduction) Hypothesis

In this hypothesis the reason for the higher ozone concentration on the weekend is due to a decrease in weekend NO_X emissions. As described above the areas that experience the higher weekend ozone levels are believed to be in a VOC-limited condition, and reducing the non-limiting precursor, NO_X, increases the amount of ozone formed. Ideally, to test this hypothesis the weekend emissions would show the same temporal and spatial patterns as during the weekends, but would be less. Unfortunately this is not the case. Several studies have shown decreases in NO_X on weekends. However, the studies have also shown, as does common experience, that the timing of the emissions and the spatial distribution of the emissions are significantly different between weekday and weekend days. This confounds the analysis of this hypothesis.

2) NO_X-Chemistry (NO_X-Timing) Hypothesis

According to this hypothesis, a difference in the timing of the NO_X emissions is the primary cause of higher weekend ozone. Without a morning rush hour on weekends, Saturday and Sunday NO_X emissions during mid-morning are much lower and VOC emissions are lower than on weekdays. On weekend mornings, fewer radicals are terminated by reaction with NO_X and the ozone formation chemistry becomes efficient earlier (compared to weekdays). As the atmosphere becomes less VOC-limited and weekend emissions begin to approach weekday levels in late morning, the fresh NO_X emissions enter an atmosphere with more efficient ozone formation chemistry (i.e., NO is rapidly oxidized to NO_2 by the primed VOC-radical cycle). Thus, a more favorable ozone forming chemistry creates the higher weekend ozone concentrations.

3) "Carryover Hypothesis"

a) Carryover at the surface

This hypothesis states that the higher weekend ozone concentrations occur because extra emissions from traffic on Friday and Saturday nights are injected into the nocturnal boundary layer. These extra emissions then lead to greater ozone formation after sunrise on the following day.

b) Carryover aloft

This hypothesis states that pollutants (primarily ozone and aged hydrocarbons) that carry over from Friday to Saturday and from Saturday to Sunday help establish initial conditions and boundary conditions that increase ozone concentrations at the surface as the weekend day unfolds.

4) "Increased Weekend Emissions" Hypothesis

According to this hypothesis, higher weekend ozone levels are caused by increased emissions from weekend activities not usually associated with weekdays. Examples include lawn mowing or recreational boating. These sources typically have very high emissions for various reasons (design, poor maintenance, age, etc.) and can possibly contribute significantly to weekend emissions.

3.2 Discussion

The following hypotheses were postulated by CARB staff to explain the Weekend Effect:

VOC-Limited (NO_X-Disbenefit/Reduction) hypothesis
NO_X-Chemistry (NO_X-Timing) hypothesis
Carryover hypotheses
Weekend Emission Increase hypothesis

These hypotheses are not necessarily mutually exclusive, as two, three, or possibly even all four may be needed to explain the weekend effect in all locations. Rather than define tasks to address these specific hypotheses, the data analyses were conducted to provide fundamental information that could be assembled flexibly to address the current and any future hypotheses.

These hypotheses represent alternative cause-and-effect explanations for observed differences in the concentrations of ozone and ozone precursors by day of week in the South Coast Air Basin. Each hypothesis is offered as a scientific proposition. The available data will be compared to the hypotheses to see which hypotheses provide a consistent explanation of the data.

The central premise of the NO_X reduction hypothesis is that transitions from Friday to Saturday and from Saturday to Sunday ***provide an empirical laboratory*** in which to observe the likely effects of a general NO_X reduction strategy. If this premise were correct, then we would expect a VOC reduction strategy in the South Coast to reduce ozone, whereas simultaneous NO_X reductions will erode the benefits of the VOC reductions. Furthermore, in the absence of VOC reductions, we would expect NO_X reductions to increase ozone concentrations.

The central premise of hypotheses 2, 3, and 4, is that transitions from Friday to Saturday and from Saturday to Sunday ***do not provide an empirical laboratory*** in which to observe the likely effects of a general NO_X reduction strategy. According to these hypotheses, emissions on weekend days differ in important respects; these differences strongly affect ozone production apart from any overall NO_X reductions. If one or more of these three hypotheses is correct, then a combined strategy of VOC and NO_X reductions may be most effective in maintaining the rapid rate of progress achieved in recent years in the South Coast. Figure 3 provides a conceptual model of the difference between short-term (diurnal and day of week) changes in ozone precursors and long-term (emission control strategies) changes in ozone precursors.

3.2.1 VOC-Limited (NO_X-Disbenefit, NO_X-Reduction) Hypothesis

3.2.1.1 Theory

This hypothesis has also been known as the “NO_X-Disbenefit Hypothesis”. According to this hypothesis, the overall VOC/NO_X ratio is the dominant factor influencing daily ozone concentration. The basin currently is characterized by a low VOC/NO_X ratio, indicating that the basin is primarily “hydrocarbon-limited” or “hydrocarbon-sensitive.” On weekends, NO_X is reduced substantially more than VOCs leading to a significantly higher VOC/NO_X ratio and the higher VOC/NO_X ratio leads to higher ozone concentrations.

The photochemical production of ozone from VOCs and NO_X has been studied extensively. It is well known that ozone producing systems are nonlinear, that is that a change in the amount of ozone produced is not directly proportional to the changes in precursor concentrations. Simple EKMA diagrams, such as the schematic example in Figure 1, illustrate the nonlinear relationships and indicate two general sets of conditions. When VOC/NO_X ratios are low, we expect benefits from VOC reductions and disbenefits from NO_X reductions. However, when VOC/NO_X ratios are high, we expect benefits from NO_X reductions and a neutral response to VOC reductions.

The basic reason for the shape of the ozone isopleths in an EKMA diagram is that NO_X participates in reactions that compete with one another. NO_X participates in radical propagation reactions that enhance ozone formation and in radical termination or "quenching" reactions that retard ozone formation. The VOC/NO_X ratio helps determine whether NO_X behaves as a net ozone generator (benefits result from NO_X reductions) or a net ozone inhibitor (disbenefits result from NO_X reductions).

Sample reactions in which radicals recycle NO to NO_2 so the NO_2 can undergo photolysis and generate ozone are shown in the following equations.

(Prominent in chemistry when reducing NO_X reduces ozone)

$RO + NO \Longrightarrow R + NO_2$

$RO_2 + NO \Longrightarrow RO + NO_2$

(where R is an organic molecule)

A sample reaction in which a hydroxyl radical is terminated by NO_2 and thus removing both the radical and the NO_2 from the ozone generating system.

(Prominent in chemistry when reducing NO_X increases ozone)

$OH + NO_2 \Longrightarrow HNO_3$

3.2.1.2 Expectations

VOC/NO_X ratios should be in the VOC-limited region.

Ozone concentrations at sunrise should be below global background levels (0.03 - 0.04 ppm) and should increase more rapidly on weekends than weekdays in areas with morning commute periods.

3.2.2 NO_X-Chemistry (NO_X-Timing) Hypothesis

3.2.1.3 Theory

According to this hypothesis, a dramatic difference in the timing of NO_X emissions is the primary cause of higher weekend ozone. If, in fact, the timing of NO_X emissions on weekend days is radically different from the timing on weekdays, the ozone production from mid-day NO_X emissions may be greatly increased. According to this hypothesis, higher weekend ozone concentrations may result from lower NO_X emissions primarily because of the timing of these emissions. Conversely, if NO_X emissions were proportionally lower for all hours of the day, as would likely occur under a general NO_X reduction strategy, this hypothesis suggests that weekends would not experience ozone increases relative to weekdays.

Hypothetically, low NO_X in the hours between sunrise and 10:00 to 11:00 a.m. allows the generation of radicals and ozone without NO_X "quenching". By mid-day on weekends, the photochemistry becomes NO_X-limited whereas weekday photochemistry still has an excess of NO_X during the mid-day hours. When weekend NO_X emissions increase during the mid-day hours, they would quickly convert to NO_2 and undergo photolysis leading to higher ozone. This general phenomenon is well-known in smog chamber studies (see Figure 2).

3.2.1.4 Expectations

Morning traffic activity should be less on weekends than on weekdays but mid-day traffic activity on weekends should be similar to that on weekdays

Weekend mornings should have lower NO_X concentrations but similar or higher concentrations during the photochemically active mid-day hours compared to weekdays

During the course of a day, the photochemistry should become NO_X-sensitive because NO_X is removed much faster than VOC from the atmospheric system. Even if VOC/NO_X ratios remain constant, as emissions decrease, photochemistry seems to shift toward more NO_X-sensitive conditions (Lu and Chang, 1998)

3.2.3 Carryover" Hypotheses

Two hypotheses are proposed under the "carryover" banner.

3.2.1.5 Carryover in the Boundary Layer

3.2.1.1.1 Theory

This hypothesis states that the higher weekend ozone concentrations occur because extra emissions from traffic on Friday and Saturday nights are injected into the nocturnal boundary layer. These extra emissions then lead to greater ozone formation after sunrise on the following day.

3.2.1.1.1 Expectations

Traffic (perhaps, from 6 p.m. to 2 a.m.) and ambient concentrations of CO, NO_X, and hydrocarbons in the pre-sunrise hours should be greater on Friday and Saturday evenings and Saturday and Sunday mornings at many sites compared to other days of the week.

3.2.1.6 Carryover in Layers Aloft

3.2.1.1.1 Theory

This hypothesis states that pollutants (primarily ozone and aged hydrocarbons) that carry over from Friday to Saturday and from Saturday to Sunday help establish initial conditions and boundary conditions that increase ozone concentrations at the surface as the day unfolds.

Hypothetically, pollutants carried over through horizontal or vertical advection have been NO_X limited for many hours because NO_X is depleted more quickly than VOC's during the course of a day. Much of the ozone that is carried over is the product of NO_X limited photochemistry during the late afternoon hours. On weekdays, the formation of ozone aloft during the late afternoon is not registered by surface-based monitoring because fresh NO from the afternoon commute activities depresses the concentrations near these monitors.

Following sunrise, ozone and precursors carried over aloft mix with "today's" pollutants as mixing heights rise. Similarly, a contaminated air mass may return from horizontal displacement so that the fresh emissions today are mixed into it; that is, fresh emissions are mixed into a NO_X-limited system. On weekdays, the fresh NO emissions overwhelm the carryover component and the system becomes VOC-limited. On Saturday or Sunday, however, the fresh emissions are reduced and the carryover component strongly affects "today's" photochemistry, making Saturday relatively NO_X-limited and Sunday even more so.

3.2.1.1.1 Expectations

Any evidence of carryover aloft should be NO_X-limited or aged hydrocarbons.

Ozone measurements aloft should routinely indicate reservoirs of ozone from 200 to 1200 meters aloft and the generation of fresh ozone aloft following sunrise before the carryover component is mixed with fresh emissions and ozone from the surface layer.

3.2.1.7 "Increased Weekend Emissions" Hypothesis

3.2.1.1.1 Theory

According to this hypothesis, higher weekend ozone levels are caused by increased emissions from certain weekend activities. If this hypothesis is to explain weekend increases in ozone, then the hypothetical emissions increase must occur at most locations in the basin. At least two emission categories – diurnal evaporative emissions and emissions from home maintenance activities – may qualify as ubiquitous. However, routine HC data may not be sufficient at present in space and time to determine whether a weekend increase in HC emissions actually occurs throughout the basin. The routine NO_X data do not indicate a general NO_X decrease rather than an increase at all hours on weekend days compared to weekdays.

Although this hypothesis may not apply generally, ozone at selected sites might reflect local increases in precursors due to weekend increases in some activities.

3.2.1.1.1 Expectations

Several “activities” should increase VOC emissions (and NO_X to a lesser extent) on weekends compared to weekdays – these activities include diurnal evaporatives, home maintenance, and recreation, (e.g., motorcycles, boating, barbecues).

3.3 Conceptual Framework

Figure 4 presents a conceptual framework that may be useful for organizing data and designing further studies. The inventory data at the left side of the diagram in Figure 4 are taken from a recent Almanac published by the ARB and represent the best information available at that time. Later inventories may alter these data with more reliable values. The air quality data in 1995 for VOC’s and NO_X are approximate values based on data from the LA - N. Main and Azusa monitoring sites. In the diagram, the “data” in 1990 and 1985 are computed using the inventory changes and VOC/NOx rations are developed from the computed values.

The diagram in Figure 4 may help suggest sampling approaches for filling critical data gaps. For example, VOC and NO_X data for multiple sites representing different subregions of the South Coast Basin are desirable to see whether trends behave according to theoretical expectations. At each site, daily sampling (rather than every n^{th} day) will greatly increase the precision with which days of the week are compared to one another. Furthermore, hourly resolution for both VOCs and NO_X will probably be needed to decide between alternative hypotheses.

Figure 4 also suggests certain questions when evaluating the implications of data with respect to each hypothesis; questions include the following:

How does the hypothesis explain trends by day of week (e.g., 1980 to 1998)? Slower progress on weekends in the last 10 years? Slow progress when NO_X reductions were slight but fast progress when NO_X reductions were substantial (according to inventory numbers)?

How does the hypothesis explain differing diurnal profiles in ozone by day of week?

How does the hypothesis explain the differences or similarities in day-of-week profiles in different subregions of the Basin?

Figure 1
Nonlinear Ozone Isopleths
(Schematic EKMA Diagram)

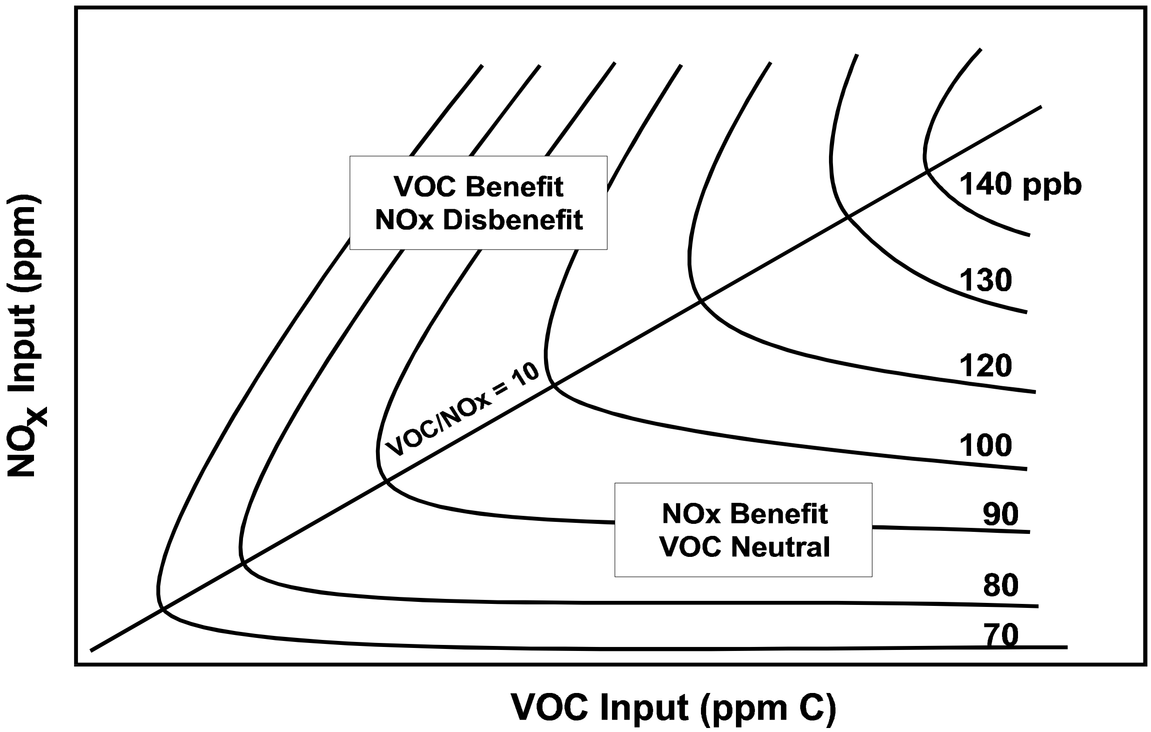
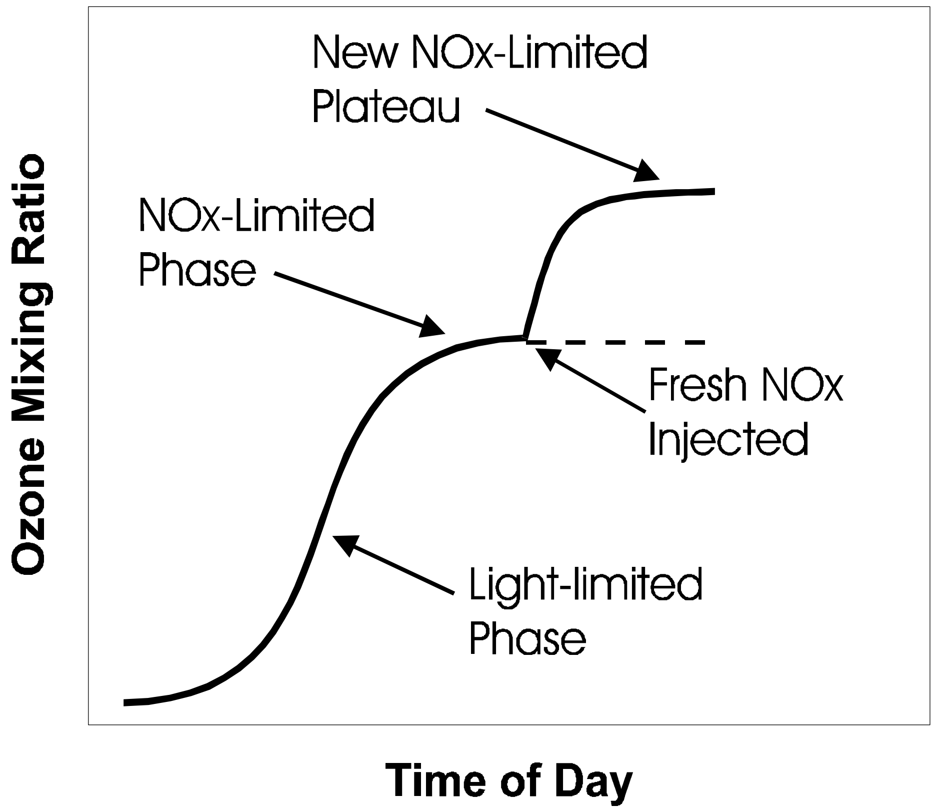


Figure 2. General Character of Laboratory Results for Experiments Concerning Timing of NOx



Source: Hess, Carnovalo, et al

Figure 3. Diurnal Emissions Profiles Before and After Implementing a NOx Control Strategy
(compared to a Sunday profile)

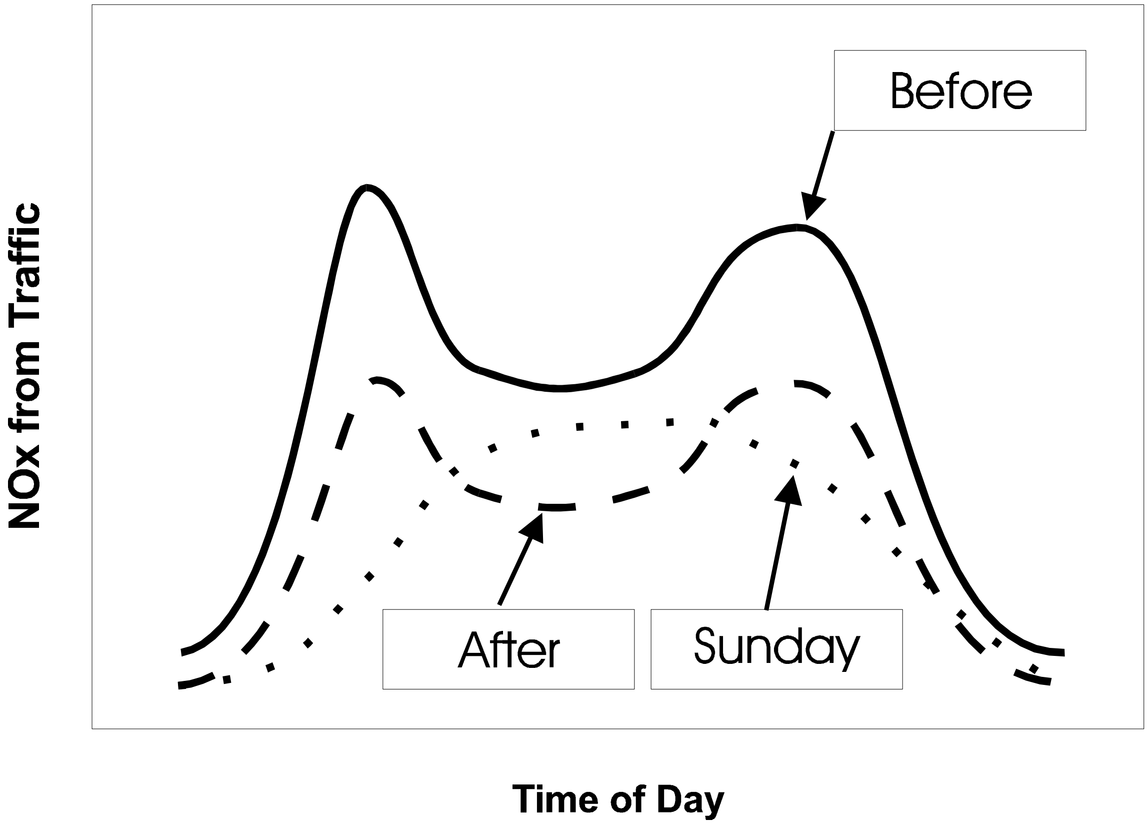
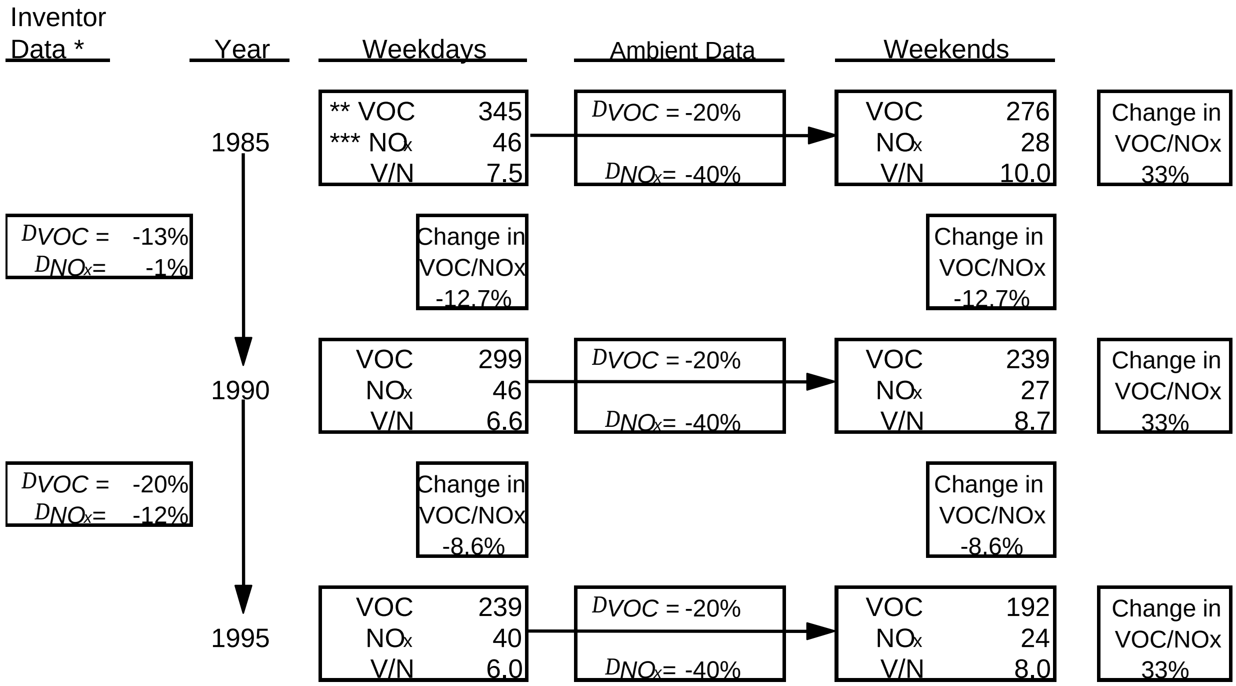


Figure 4. Conceptual Structure of Air Quality and Emissions Inventory for the South Coast Air Basin



* Based on total emissions for the South Coast Air Basin from the 1999 California Almanac of EMISSIONS & AIR QUALITY

** VOC data in ppbC loosely based on data for the L.A. - North Main and Azusa monitoring sites

*** NOx data in ppb loosely based on data for the L.A. - North Main and Azusa monitoring sites