CHAPTER 3

KEY FINDINGS IN THE SCIENCE OF OZONE POLLUTION:
What has Science Learned that Policy-Makers Should Know?

Over the past decade, a more accurate and complete understanding of the phenomenon of O₃ pollution in North America has been developed. These advances have been documented in the Critical Review Papers commissioned by NARSTO (listed in the Preface) and in other open literature. Examples of significant advances and the Critical Review Papers that describe them include:

Increased resolution and sophistication of chemical and meteorological measurement technologies (CR3; CR4; CR5)

Improved understanding of the underlying processes that foster the production, accumulation, transport, and removal of O₃ (CR14; CR15; CR16; CR21; CR22; CR23; CR24)

Development and improvement of computers and algorithms used to simulate these processes (CR17; CR18; CR19; CR20)

Enhancement of national air-quality monitoring networks in North America (CR2)

Performance of urban and regional-scale air pollution field experiments (CR6; CR13)

Development and improvement of diagnostic and observation-based methods allowing scientists to analyze data from these networks and experiments in new and innovative ways (CR1; CR7; CR8; CR9; CR10; CR11; CR12; CR13)

This Chapter presents a focused summary of recent scientific and technical advances related to O₃ pollution in North America, emphasizing advances in understanding and capabilities believed to be most relevant for the policy makers. The specific topics discussed are listed in the Textbox above. The presentations are organized as a series of Policy-Relevant Issues and Findings. Discussion and documentation are provided to support the findings and summarize the scientific progress. A statement of policy relevance and a list of the issues considered are provided at the beginning of each section.
3.1 O₃ TRENDS: What’s Happening And Why?

Attempts to mitigate O₃ pollution across North America through directed reductions in precursor emissions were initiated in the 1970s. How successful have these emission controls been? This question is addressed here by reviewing the scientific evidence related to O₃ trends in North America and the possible relationship to trends in O₃ precursor concentrations and emissions.

3.1.1 Issue: What are the sources of data for discerning decadal trends in O₃ over North America?

Finding: Data are obtained from O₃ monitoring networks in North America that are largely urban in character and limited to surface measurements.

Discussion: Long-term data on O₃ concentrations over North America are available from two sources: 1) surface monitoring sites where O₃ is measured on a continuous basis and 2) ozonesonde sites where vertical distributions of O₃ are measured using balloons that are launched on a periodic basis (e.g., weekly). Each type of measurement has advantages and disadvantages. Surface measurements provide a continuous record in time but no vertical information. Since the “continental background” concentration for O₃ over North America is determined largely by the O₃ abundance above altitudes greater than 1 to 2 km (see Levy et al., 1997), surface sites are not well suited for characterizing continental background O₃ concentrations and trends. Ozonesondes, on the other hand, provide quasi-instantaneous, vertical snapshots of O₃ concentration but, because of the relatively high costs of their deployment, provide data at low time resolution (i.e., typically a measurement every few days to a week). Because both surface and vertical measurements represent concentrations only in the close proximity of their respective sampling sites, spatially disperse measurement networks are required to document O₃ distributions. A third type of data source, still in development, applies remote sensing of O₃ from surface- or space-based platforms. Remote sensing could provide data with significant horizontal, vertical, and temporal coverage and resolution.

However, existing space-based systems have limited ability to characterize tropospheric O₃ concentrations and distributions (e.g., Fishman et al., 1996) and surface-based instruments have not been integrated into monitoring networks to any appreciable extent.

Figure 3.1 illustrates the locales of long-term surface O₃ monitoring sites and ozonesonde sites in North America. Data from the Canadian sites are archived and accessible through the National Air Pollution Surveillance (NAPS) Program coordinated by Environment Canada; the U.S. data are accessed through the Aerometric Information Retrieval System (AIRS) maintained by the U.S. EPA. Mexican data can be found at www.ine.gob.mx/dggia/indicadores/ingles/ca2_32.htm.

Figure 3.1 indicates a fairly extensive network of surface sites, especially in the United States and the southern part of Canada. Because of the historical focus on O₃ pollution in major metropolitan centers, the network is dominated by monitoring sites in urban and suburban locales. Sites designated as urban or suburban outnumber sites with a rural designation by about 2:1 (Table 3.1). The designation given to many monitoring sites in the United States reflects the land use in the immediate vicinity of the site and...
Figure 3.1 Locations and designations of surface $O_3$ monitoring sites (after CR1) and ozonesonde sites (after Tarasick et al. 1995; Oltmans et al., 1998) in North America. Note that three North American ozonesonde sites, two in Canada (Resolute and Alert, Nunavut Territory) and one in the United States (Barrow, Alaska) are too far north to appear on the map. The ozonesonde site in California and the surface sites outside of Mexico City were initiated in the 1990s and thus have not yet gathered a sufficient database to establish trends. Moreover, as discussed in the text, the “rural” designation for many of the surface sites in the United States may not accurately reflect the true nature of the land use at that locale.

may not accurately reflect $O_3$ features surrounding the site. There are, at present, no strict federal criteria for assigning a “rural” designation for a site in the United States and the determination is usually made by the state or local air-quality management authority responsible for the site maintenance. Since most $O_3$ monitoring sites in the United States are within or downwind of urban areas, most of the rural sites are close enough to urban source areas to be significantly affected by urban pollutant plumes (CR2). Consequently, sites designated as rural may not reflect prototypical air quality over a broad spatial extent. Data from ozonesondes in North America are currently limited to nine sites, with the California site activated only recently, in 1997. Thus, while we can report $O_3$ trends in many urban locales with a high degree of confidence, our ability to do the same for rural areas and for the continental background is highly limited. This deficiency will become especially critical if, as described in Section 3.8, new $O_3$ standards and goals force an expansion of the regulatory focus to include the non-urban environment and to bring $O_3$ concentrations closer to the continental background.

3.1.2 Issue: What is the decadal trend in $O_3$ over North America?

Finding: No single pattern for trends in $O_3$ over North America emerges from analyses of $O_3$ monitoring data.

Discussion: $O_3$ trends (i.e., the percent change in $O_3$ concentration per year) are reported using a variety of metrics. These range from a simple measure of the average change in $O_3$ concentration at a given site over some period to more complex metrics that correct for meteorological and other variables (e.g., compare left and right panels of Figure 3.2). Trends also can be reported for clusters of sites instead of

For example, the monitoring site in Tucker, Georgia is designated as “rural”, but is only 20 km northeast of downtown Atlanta, a metropolitan area with a population of approximately 3 million people.
individual sites (e.g., Figure 3.3). Because the North American nations do not report O₃ trends using a common metric or use a common method for removing meteorological variability, comparing trends reported by the three nations can be problematic. The development of a common protocol for archiving data from air-quality monitoring sites in North America and the trends derived from these sites would appear to be a useful goal for future NARSTO collaboration.

Analysis of data collected since the 1980s reveals local and regional O₃ trends that vary considerably with locale and land use (CR1). Specifically:

- In the United States, the average daily maximum 1-hr O₃ concentration recorded at surface monitoring sites has decreased by about 15% over the decade ending in 1996 (see Figure 1.3). However, Figure 3.2 shows considerable spatial variability in this trend, with AIRS-designated urban and suburban sites generally showing larger decreases than AIRS-designated rural sites. In fact, Fiore et al. (1998) report that the most significant negative trends in O₃ during the period 1980-1995 are clustered in the three largest metropolitan areas of the United States — Los Angeles, New York, and Chicago — and that less than 15% of the AIRS sites that were truly rural had a significant downward trend in either the 90th percentile or median O₃.

- Trends in meteorologically adjusted daily maximum O₃ concentrations in Canada appear to be distinctly different from those of the United States, with urban/suburban areas generally showing increases and rural areas decreases (Canadian - Data, 1997). However, as is the case for the United States, Canadian trends show significant spatial variability, with the Vancouver region, the Atlantic provinces, and Ontario experiencing increasing trends in peak O₃ of 0.45 (1985-1992), 2.2 (1985-1992), and 1.2 (1980-1990) %/year, respectively, and Montreal a decreasing trend of 0.87 %/year from 1981-1993 (see Figure 3.3).

- In Mexico City, the only Mexican locale with a long enough data record to infer a trend, peak O₃ concentrations have been fairly constant since the early 1990s (see Figure 1.4).

- Very sparse ozonesonde data suggest that free-tropospheric O₃ over North America since the 1980s has been either constant or slightly decreasing (SPARC/IOC Ozone Trends Panel, 1998; Oltmans, et al., 1998; Tarasick et al., 1995).

The surface O₃ trends discussed above represent changes in the O₃ concentrations observed at fixed locations, over a period when concurrent VOC and NOₓ emissions may have changed significantly, either because of economic growth or from precursor mitigation efforts. However, as discussed in Section 3.2, local changes in the VOC/NOₓ ratio can shift the geographical locations of peak O₃ concentrations. Thus the O₃ trends inferred from the existing surface networks may not reflect behavior of peak O₃ concentrations within a given urban area and/or region.
3.1.3 Issue: What are the sources of data for discerning and verifying decadal trends in O$_3$ precursors over North America?

Finding: Long-term monitoring data for O$_3$ precursors, VOC and NO$_x$, are relatively sparse and thus provide limited information on VOC and NO$_x$ trends.

Discussion: Emission inventories are used to characterize and quantify the sources of VOC and NO$_x$ in a region and their changes over time as a result of O$_3$ mitigation efforts. Data on the ambient concentrations of VOC and NO$_x$ can represent a valuable resource for evaluating and verifying these inventories. Unfortunately, the database on the concentrations of O$_3$ precursors over North America is limited (CR2). The longest record for these species is for the Los Angeles area, where a network of NO$_x$, total hydrocarbon, and methane monitors was first deployed in the early 1960s. Reasonable data records also exist for some cities in the eastern United States.
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3.1 Trends in 8-hr Averaged O₃ vs. 1-hr Averaged O₃: How Do They Compare?

Recent controlled human and chamber studies have been interpreted to indicate that significant health effects can result from multiple-hour exposures to moderate O₃ concentrations. As a result, new policies have been promulgated or are being considered to limit this type of exposure. (For example, the United States has promulgated an 8-hr, 80-ppb NAAQS.) These changes, in turn, raise an important issue related to O₃ trends. Historically, air-quality O₃ trends have been reported for the 1-hr averaged concentration. How do trends in 8-hr O₃ concentrations compare to these 1-hr averaged trends?

Analyses of O₃ data from the U.S. AIRS sites suggest that the decadal trends in O₃ concentrations averaged over 8 hours are likely to be smaller than those calculated for 1-hr averages. For example, for the decade ending in 1996, the decrease in the AIRS composite average of 8-hr, fourth-highest daily maximum O₃ concentration was reported by the U.S. EPA (1998) to be 11%, or about one-third smaller than the 15% decline reported for the AIRS composite 1-hr metric. In another study Korsog and Wolff (1996) found little to no downward trend in 8-hr O₃ levels in most of urban areas of the eastern United States, in direct contrast to significant declines in 1-hr O₃ levels in most of the same urban areas during about the same 10-year period. Thus it would appear that, if the downward urban O₃ trends reported for the United States are due to emission controls, these controls have had less effect on 8-hr averaged concentrations at a given location than they had on the equivalent 1-hr averaged concentrations.

In Canada, measurements of urban NOₓ began in 1980, and non-methane hydrocarbons (NMHC) in 1989. Measurements of NOₓ in Mexico City began in 1990 and in later years in other Mexican cities and thus are not yet adequate to discern trends.

In addition to the sparseness of the O₃ precursor database, other serious data limitations exist. All of the long-term measurements of VOC and NOₓ in North America are ground-based. This is of some concern, since limited balloon and airborne precursor measurements acquired during special, intensive field studies indicate that vertical profiles of these compounds can be quite complex and variable (CR13; Andronache et al., 1996). Furthermore, long-term VOC and NOₓ monitors are situated largely at urban or urban-influenced sites. Other concerns are the unavailability of long-term oxygenated organic-compound measurements (e.g., formaldehyde) and the documented lack of sensitivity and specificity of the NOₓ instrumentation used at most monitoring sites to measure NO and NO₂ (see Section 3.6). A new monitoring network, the Photochemical Assessment Monitoring Stations (PAMS) initiated in the United States in 1993, has the potential to address some of the above limitations, provided that it is properly equipped, maintained, and quality assured (Section 3.6).

3.1.4 Issue: Are decadal trends in O₃ precursors over North America consistent with the expectations from the imposition of emission controls?

Finding: Limited data indicate generally downward trends in urban O₃ precursors, an observation that is qualitatively consistent with urban emission inventories.

Discussion: Figure 3.4 illustrates the trends, estimated from existing emission inventories, of VOC and NOₓ emissions from the United States. These inventories indicate a decrease in anthropogenic VOC emissions of 18% over the decade ending in 1996, and an increase in NOₓ emissions by 3%. A major feature influencing both trends is the decreasing contribution from the transportation sector, in large part as a result of emission controls imposed on light-duty vehicles (see Textbox 3.2).
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Given the sizable decrease in overall VOC emissions in the U.S. inventory, one would expect to find evidence of a significant decrease in urban U.S. VOC concentrations. Limited existing data generally support this expectation. For example, in Los Angeles, summertime morning NMHC concentrations are reported to have decreased by 25% from 1987-1992 (Fujita, 1995), while in northeastern U.S. cities they have decreased by about 30% or more from 1986 - 1991 (U.S. EPA, 1998).

The situation for urban NO$_x$ is more complex. While total NO$_x$ emissions in the United States are estimated to have increased by 3%, the transportation component decreased by 6%. Since urban NO$_x$ emissions are often dominated by mobile sources, it is perhaps reasonable to expect to find evidence of decreasing urban U.S. NO$_x$ concentrations. In general, this expectation is also borne out. Annual mean NO$_2$ ambient concentrations for the decade ending in 1996 showed a 10% decline (U.S. EPA, 1998). However, there is some spatial variability in this trend, with Los Angeles sites showing an average summertime decrease of about 25% and the northeastern cities reporting virtually no change.

In Canada, inventories indicate a decrease in VOC and NO$_x$ emissions from the transportation sector of 25% and 21%, respectively, over the period from 1990 and 1995, but essentially constant total emissions when contributions from all sectors are considered (Canadian - Data, 1997). Ambient measurements in Canada show a significant downward trend in urban NO$_x$ concentrations (see Figure 3.6), suggesting that, like urban NO$_x$ in the United States, urban NO$_x$ in Canada is more closely tied to mobile sources than to total emissions. Ambient measurements of urban VOC, on the other hand, show no significant trend (see Figure 3.7), perhaps because of the shortness of the data record and the large short-term variability in the data.

![Figure 3.4 Estimated annual anthropogenic U.S. emissions of VOC and NO$_x$ by sector. After U.S. EPA (1997).](image-url)
3.2 What Would Have Happened Without Mobile Source Controls?

Over the past decades, Canada and the United States have undertaken programs to reduce \( \text{O}_3 \) precursor emissions from automobiles. Major emission reductions in both VOC and \( \text{NO}_x \) emissions resulted. For example, a light-duty vehicle manufactured in the United States in 1993 emits only a few percent of the VOC and 10 to 25\% of the \( \text{NO}_x \) that came from autos built before the introduction of controls (see Table 3.2). With continuous fleet turnover, increasing the percentage of modern vehicles on the road, as well as mandated reductions in fuel volatility and reactivity and on-board engine diagnostics, VOC and \( \text{NO}_x \) emissions in Canada and the United States from the transportation sector are estimated to have declined significantly over the past 10 years (e.g., see Figure 3.4). These declines are especially impressive given the sizable increase in vehicle usage (e.g., vehicle kilometers traveled, VKT) over the same time period.

It is interesting to speculate what urban \( \text{O}_3 \) levels might be like in Canadian and U.S. cities had there been no mobile-source emission controls. Harley et al. (1997) examined such a scenario for the Los Angeles area, where VKT more than doubled between 1960 and 1987. These investigators used an air-quality model to examine the impact of an uncontrolled vehicle fleet with 1987 traffic volumes on \( \text{O}_3 \) concentrations in the Los Angeles area during a 1987 air pollution episode studied during the Southern California Air Quality Study. Figure 3.5 compares the predicted maximum 1-hr average \( \text{O}_3 \) concentrations for the uncontrolled fleet with that predicted for a controlled fleet. The simulation using the uncontrolled fleet produced major \( \text{O}_3 \) enhancements, with concentrations significantly greater than either the actual 1987 measurements or the simulation using the controlled fleet emissions. While these results are subject to the uncertainties attendant to model simulations (see Chapter 4), they do provide a cogent case that \( \text{O}_3 \) air quality would have degraded substantially in the absence of motor vehicle control programs.

Figure 3.5  Spatial distribution in model-predicted maximum 1-hour average \( \text{O}_3 \) concentration in the Los Angeles area on August 28, 1987 using base-case emissions (top panel) and using uncontrolled-vehicle-fleet emissions (bottom panel). The white, unshaded area indicates the model domain. After Harley et al. (1997). The calculations suggest that peak \( \text{O}_3 \) concentrations in the Los Angeles area would be about twice as large (with maxima of ~ 500 ppb) in the absence of emission controls on automobiles.
3.1.5 Issue: Can we ascribe $O_3$ trend behavior to specific changes in precursor emissions?

**Finding:** It is likely that the downward trends in $O_3$ observed at many locales were caused, at least in part, by the imposition of emission controls.

**Discussion:** Significant downward trends in surface $O_3$ in some urban areas of the United States have been seen over the past decade. We cannot necessarily attribute these downward trends to decreasing precursor emissions. The relationships between $O_3$ and its precursors are nonlinear and spatially complex (see Section 3.3.2), and meteorological and climatic factors, as well as downward transport of $O_3$ from the free troposphere and stratosphere, represent confounding variables (CR1). On the other hand, downward $O_3$ trends are inferred for urban areas in the United States after correcting for meteorological variations (see Figure 3.2), and free-tropospheric $O_3$ concentrations over North America appear to have remained relatively constant over the past 10 years. Urban NO$_x$ and VOC concentrations appear to have declined over the past decade. These facts suggest that the downward trends in $O_3$ concentrations observed in some urban areas

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<th>NO$_x$ (g/mile)</th>
<th>HCs Exhaust (g/test)</th>
<th>HCs Evaporative (g/test)$^d$</th>
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$^a$ Adapted from Calvert et al. (1993)

$^b$ Standards are for 50,000 miles or 5 years (100,000 miles or 10 years)

$^c$ California standards also apply to Maine, Massachusetts, New York and Vermont. Starting at various times after 1993

$^d$ Starting in 1997 the test procedure for HC evaporative emissions was switched from a 1-hr test to a more stringent 72-hr test

$^e$ Reflects change in test procedure

$^f$ TLEV = transitional low emission vehicle; LEV = low emission vehicle, ULEV = ultra low emission vehicles. A mix of these vehicles is being phased in beginning in 1994 in order to incrementally decrease fleet average emissions through 2003.

$^g$ Phase-in of TLEVs and LEVs in 9 northeastern states in 1999 and 2000

$^h$ California LEV standards nationwide

Provisional
are in fact a response to the imposition of emission controls and are thus consistent with our understanding of the controlling factors in urban O₃ production.

In contrast to the United States, trends in Canada’s meteorologically adjusted, daily maximum urban O₃ concentrations are variable, but generally increasing. It cannot yet be determined whether the difference between the U.S. and Canadian trends is real and reflective of different precursor emission trends, or whether it is an artifact of variations in network design and operation (i.e., station number, density, location, time period, etc.) and data-analysis procedures. One explanation that has been advanced is that the urban O₃ increases in Canada occurred in response to the significant decline in urban NOₓ emissions over the period without a concomitant decline in urban VOC concentrations; i.e., the effect of the “NOₓ disbenefit” (Canadian - Data, 1997). However, this interpretation is based on a relatively short record of VOC measurements.
3.2 MANAGING OZONE WITH EMISSION CONTROLS: VOC OR NO\textsubscript{x} OR BOTH?

In the 1960s and 1970s it was believed that O\textsubscript{3} pollution could be mitigated most effectively through controls on VOC emissions (see for example, Figure 1.2). As discussed in Section 3.1, the implementation of such controls has had a mitigating influence, but attainment of O\textsubscript{3} standards and goals remains elusive. By the late 1980s, there was a growing appreciation for the potential efficacy of NO\textsubscript{x} controls in some areas. This changing viewpoint was reflected in the 1991 NRC report: “To substantially reduce O\textsubscript{3} concentrations in some ... areas ... the control of NO\textsubscript{x} emissions will probably be necessary in addition to, or instead of, the control of VOCs.” (NRC, 1991).

Since the 1991 NRC report was issued, an increasingly complex picture has emerged: there is often no simple answer to the question of whether a VOC or NO\textsubscript{x}-based strategy should be adopted. For a given O\textsubscript{3} pollution episode, O\textsubscript{3} concentrations in some portions of an affected area may be most effectively mitigated by VOC controls, while others may be most effectively mitigated by NO\textsubscript{x} controls. This complex picture and its implications for policymakers are explained in this section.

### 3.2.1 Issue: What determines the relative effectiveness of VOC and NO\textsubscript{x} controls?

**Finding:** VOC and NO\textsubscript{x} limitation is not uniquely defined by location or emissions; it is, rather, a chemical characteristic of an air parcel that varies dynamically with transport, dispersion, and photochemical aging.

**Discussion:** The relative rates at which NO\textsubscript{x} and VOC are removed from an airshed by photochemical and dynamical processes are centrally important to determining the relationship between O\textsubscript{3} and its precursors. To illustrate this fact, the results of a series of simple box model calculations done for this report are presented in Figure 3.8. In each calculation, an air parcel is assumed to have initial VOC and NO\textsubscript{x} concentrations at 0800 hours that are allowed to react over the course of a single day while mixing with relatively clean air from aloft at varying rates. While these simulations greatly simplify the complex chemical processes that lead to O\textsubscript{3} pollution, they nevertheless capture much of the essence of the relationship between O\textsubscript{3} and its precursors.

The scenario illustrated in Figure 3.8A assumes a moderate amount of vertical mixing during a typical summer day in North America. For these conditions and the high initial VOC and NO\textsubscript{x} concentrations assumed for the “Base” case, the model predicts a rapid rise in O\textsubscript{3} reaching a peak of about 130 ppb around mid-afternoon - a temporal pattern in O\textsubscript{3} that is characteristic of many moderate urban air pollution episodes in North America. (If the effects of dispersion and surface deposition were included, the...
peak concentration would have been somewhat depressed and the decay following the peak more pronounced.)

A key feature of Figure 3.8A is the varying response of $O_3$ to different initial concentrations of VOC and NO$_x$. Because of the nature of urban VOC and NO$_x$ emissions, air parcels exposed to these emissions are usually initially within the VOC-limited regime. Thus, inspection of Figure 3.8A indicates that halving the initial VOC concentration (i.e., the curve labeled “VOC/2”) is much more effective in reducing $O_3$ than halving NO$_x$ (i.e., the curve labeled “NO$_x$/2”) during the first ~ 5 hours of the simulation. In fact, during the first few hours there is an “NO$_x$ disbenefit”; that is, an increase in $O_3$ resulting from a decrease in NO$_x$. This effect results from the rapid removal of OH radicals (via (R9) in Textbox 3.3) when NO$_x$ concentrations are extremely high.

Figure 3.8A indicates that the NO$_x$ disbenefit decays with time. Moreover, soon after its disappearance, the air parcel begins to move from VOC-limitation to a transitional region between VOC- and NO$_x$-limitation, and eventually reaches NO$_x$-limitation after about 1400 (i.e., after this time, halving NO$_x$ reduces $O_3$ more than halving VOC). Another important feature of this chemical process is that the $O_3$ concentration reaches its peak when the air parcel is in the transitional region between VOC- and NO$_x$-limitation.

The central role of NO$_x$ removal in fostering this transition becomes apparent when comparing the results illustrated in Figure 3.8A with the model-calculated NO$_x$ concentration for this case in Figure 3.11. Note the rapid decrease in NO$_x$ as a function of time. Because of this rapid decrease, the VOC/NO$_x$ ratio in the parcel increases sharply, and this in turn drives the air parcel’s transition from VOC to NO$_x$ limitation. These results provide a qualitative explanation for the spatial distributions in VOC and NO$_x$ limitations that are typically found in urban areas (e.g., Figure 3.12). In and near urban cores, air parcels are exposed to fresh pollutants and thus tend to fall into the VOC-limited regime. However, in suburban and rural regions, air parcels tend to contain pollutants that have been photochemically processed. In addition to producing elevated $O_3$ concentrations, this photochemical processing fosters transitional or NO$_x$-limited chemistry.

In addition to photochemical processing, other phenomena can affect the NO$_x$ concentrations in polluted air parcels and thus can further confound the relationship between $O_3$ and its precursors. Vertical mixing is one such phenomenon. In general, the severity of air-pollution episodes is exacerbated as stagnation sets in and mixing rates decrease. Thus, Figures 3.8B and 3.8C show higher $O_3$ concentrations generated as vertical mixing is decreased. However, there is another indirect, but nevertheless important effect. As illustrated in Figure 3.11, lowering of mixing rates tends to enhance NO$_x$ concentrations, by hindering its dilution with cleaner air from aloft. For this reason, stagnation tends to slow the rate of transition from VOC to NO$_x$ limitation and extend the period of NO$_x$ disbenefit. If vertical mixing is extremely weak (i.e., conditions assumed for Figure 3.8C), the sun may set before the NO$_x$ is sufficiently processed and VOC-limitation applies throughout.

The distribution of NO$_x$ emissions also can affect where and if air parcels within a given airshed transition to VOC limitation. Like stagnation, the presence of dispersed NO$_x$ sources in a large urban area can lead to high NO$_x$ concentrations throughout the area, fostering continuous VOC limitation. The ratio of VOC to NO$_x$ emissions can also have an impact. As this ratio decreases, the chemistry is slowed, thus extending the period of VOC limitation and NO$_x$ disbenefit. In this regard it is relevant to note that VOC/NO$_x$ ratios in many urban areas in the United States have decreased from about 10 to about 6 to 7. (U.S. EPA, 1998).d

Thus, the efficacy of VOC and NO$_x$ controls at a particular location in a metropolitan area is critically dependent upon a variety of factors. Because these factors can vary from episode to episode, the benefits of VOC and NO$_x$ controls at a given locale can also be episode-dependent, as suggested by the results in Figure 3.13.
Figure 3.8 Simple model calculations illustrating the varying sensitivity of O₃ photochemical production to VOC and NOₓ for three distinct mixing regimes. In each panel, model-calculated O₃ concentrations are plotted as a function of time of day for a hypothetical air parcel containing an initial, urban-like mixture of anthropogenic VOC and NOₓ under summertime conditions with 1 ppb of biogenic isoprene and varying rates of vertical mixing and free tropospheric entrainment. For each mixing rate, simulations for three initial VOC and NOₓ concentrations are presented: “Base” with initial VOC and NOₓ = 1.5 and 0.25 ppm respectively; “VOC/2” with initial VOC = 0.75 and NOₓ = 0.25 ppm; and “NOₓ/2” with initial NOₓ = 0.125 and VOC = 1.5 ppm. Note the characteristic tendency for the system to evolve from VOC-limitation to NOₓ-limitation with time and for the point of transition to be delayed as mixing decreases.
A schematic of the photochemical smog mechanism is presented in Figure 3.9. O₃ production (the red lines in the figure) occurs via the free-radical-initiated oxidation of VOC or CO in the presence of NOₓ (= NO + NO₂) and sunlight. For example,

\[
\begin{align*}
(R1) & \quad RH + OH \rightarrow R + H₂O \\
(R2) & \quad R + O₂ + M \rightarrow RO₂ + M \\
(R3) & \quad RO₂ + NO \rightarrow RO + NO₂ \\
(R4) & \quad RO + O₂ \rightarrow HO₂ + carbonyl \\
(R5) & \quad HO₂ + NO \rightarrow OH + NO₂ \\
(R6) & \quad 2x(NO₂ + hν \rightarrow NO + O) \\
(R7) & \quad 2x(O + O₂ + M \rightarrow O₃ + M)
\end{align*}
\]

NET: \( RH + 4O₂ + 2 hν \rightarrow \text{carbonyl} + H₂O + 2O₃ \)

where RH represents a generic hydrocarbon, R is a hydrocarbon chain (e.g., CH₃CH₂ for RH = ethane), and M is a third body (N₂, O₂). The carbonyl compound produced in the sequence is in general subject to further oxidation that can lead to the production of additional O₃. Of note in this sequence is that VOCs are consumed, while both OH/HO₂ and NOₓ act as catalysts. Termination occurs when the catalysts are removed, often by one of two paths:

\[
\begin{align*}
(R8) & \quad HO₂ + HO₂ + M \rightarrow H₂O₂ + O₂ + M \\
(R9) & \quad OH + NO₂ + M \rightarrow HNO₃ + M
\end{align*}
\]

In general, the rate of O₃ production can be limited by either VOC or NOₓ. The existence of these two opposing regimes, often schematically represented in an EKMA diagram (Figure 3.10), can be mechanistically understood in terms of the relative sources of OH and NOₓ (Kleinman et al., 1994; CR8). When the OH source is greater than the NOₓ source, termination is dominated by (R8) (the blue line in Figure 3.9). Under these conditions, the formation of H₂O₂ >> the formation of HNO₃, NOₓ is in short supply, and as a result the rate of O₃ production is “NOₓ-limited”. This means that O₃ concentrations are most effectively reduced by lowering the emission/concentrations of NOₓ instead of VOC. When the OH source is less than the NOₓ source, on the other hand, termination proceeds predominantly via (R9) (the green line in Figure 3.9), the formation of HNO₃ >> the formation of H₂O₂, NOₓ is relatively abundant, and O₃ production is VOC-limited (i.e., O₃ is most effectively reduced by lowering VOC). Finally, between these two extremes (i.e., the NOₓ- and VOC-limited regions), lies a transitional region, sometimes referred to as the ridge in an EKMA diagram. In this transition region, O₃ is about equally sensitive to VOC and NOₓ, but, compared to its sensitivity to VOC in the VOC-limited region and its sensitivity to NOₓ in the NOₓ-limited region, relatively insensitive to both.

There are a variety of chemical parameters used to diagnose whether an air parcel is in the NOₓ-limited or VOC-limited regime. In the early years of O₃ pollution research, the VOC to NOₓ ratio was often used. Other parameters of more recent pedigree and generally greater diagnostic power include the Extent of Reaction (Johnson and Quigley, 1989; CR9), Photochemical Indicator ratios (Sillman, 1995), the Relative Incremental Reactivity and related reactivity factors (Carter and Atkinson, 1987), and the Photochemical Ozone Creating Potential (Derwent and Jenkin, 1991). In general, there is a qualitative equivalency between all of these parameters (see Section 3.7).
Figure 3.9  Schematic of the photochemical pathways leading to the production of O₃ (red lines) and the termination steps that dominate under NOₓ-limited (blue line) and VOC-limited (green line) regimes.

Figure 3.10  Isopleths of 1-hour maximum O₃ concentrations (in ppm) calculated as a function of initial VOC and NOₓ concentrations and the regions of the diagram that are characterized by VOC- or NOₓ-limitation.
Figure 3.12 A classic illustration of how O₃ sensitivity to VOC and NOₓ within an urban area changes with location based upon a model simulation of a 2-day episode in August 1992 in the Los Angeles area. The center graphic is a map of the model area; the left-hand graphic is the predicted distribution in the peak O₃ concentration (in ppm) for the base case (i.e., without emission reductions); and the graphics surrounding the map are isopleths of peak O₃ concentrations (in ppm) predicted for varying levels of VOC and NOₓ emission reductions at locations across the Los Angeles basin: (a) Downtown Los Angeles; (b) Pasadena; (c) San Bernardino; (d) Chino; (e) Rubidoux. The model predicts a range of responses to emission reductions, with peak O₃ being most effectively reduced by VOC controls in and around the downtown Los Angeles area (where populations are generally most dense) and most effectively reduced by NOₓ controls in the more outlying areas (where peak O₃ concentrations tend to be higher). After Milford et al. (1989).
3.2.2 Issue: Are there general guidelines for policy makers regarding VOC- and NO\textsubscript{x} -based O\textsubscript{3} abatement strategies?

Finding: Rules-of-thumb can be outlined, but an optimal strategy for a specific locale/region will depend upon the specific characteristics of the locale/region and on the policy priorities identified for the abatement program.

Discussion: A synthesis of results from field studies and model simulations (CR6, CR7, CR8, CR9, CR10, CR11, C13, and CR19) suggests general rules for optimizing an O\textsubscript{3} abatement strategy. These include:

- For O\textsubscript{3} abatement programs focused on the urban core where population densities are usually the greatest but where O\textsubscript{3} concentrations are often not the largest, a VOC-based strategy will frequently be most effective. An important exception to this rule is in urban areas where natural VOC concentrations are large. In these cases, a NO\textsubscript{x}-based strategy may be required even though the chemistry is VOC-limited (see Section 3.4). Other possible exceptions include cases in which most of the O\textsubscript{3} in the urban core is transported from upwind, or in cases where “recirculation” of aged local pollution contributes significantly to O\textsubscript{3} in the urban core (e.g. Jacobson et al., 1996; Lu and Turco, 1996, St. John and Chameides, 1997).

- For O\textsubscript{3} abatement programs focused on regional air quality, a NO\textsubscript{x}-based strategy will probably be most effective.

Figure 3.13 Optimal control strategies for a given urban area can change from one episode to another. Illustrated here are the Relative Incremental Reactivities (RIR) of nitric oxide (NO) and anthropogenic hydrocarbons (AHC) for the Atlanta Metropolitan Area for the average of 6 summer O\textsubscript{3} episode days during 1990 and for one of those 6 days (i.e., August 21, 1990). These RIRs were inferred using the Observation Based Model (OBM) of Cardelino and Chameides (1995) driven by measured concentrations of speciated hydrocarbons, NO, and O\textsubscript{3}. The bars indicate the percent reduction in O\textsubscript{3} for each percent reduction in NO or AHC and the vertical lines above the bars indicate the standard error in the mean for each percent reduction. The OBM results suggest that O\textsubscript{3} concentrations in Atlanta can be most effectively reduced, on average, by NO emission reductions, but that episodes can occur (e.g., August 21, 1990) when VOC emission reductions would be more effective. (CR11).

\textsuperscript{a} It is believed that the decrease in the VOC to NO\textsubscript{x} ratio in the United States reflects the large reductions in VOC emissions relative to those of NO\textsubscript{x} over the past decade.
• O₃ abatement strategies focused on lowering peak O₃ concentrations in and around urban areas present the most complex situation. As outlined above, peak O₃ concentrations can be generated under a variety of meteorological conditions and emission distributions, and these can affect the relationship between the peak O₃ and its precursor emissions. Consider, for example, the following two scenarios:

**Scenario 1: An urban O₃ episode with significant advection of polluted air parcels from the urban-core source region to suburban and outlying rural areas with significantly lower pollutant emissions.** Under these conditions, the region where peak O₃ concentrations occur generally will be characterized by the transitional regime of the chemistry between VOC- and NOₓ-limited conditions. However, whether a given (often suburban) locale in the general vicinity of the peak O₃ concentration is on the VOC-limited or NOₓ-limited side of this transition likely will vary from episode to episode, depending upon meteorological conditions and emission distributions. For these reasons, abatement strategies for the locales where the peak O₃ concentrations are found likely will require both VOC and NOₓ emission controls.

**Scenario 2: An urban O₃ episode with strong stagnation in an area with disperse pollutant sources throughout the suburban as well as urban core.** Under these conditions, high NOₓ concentrations are likely to be maintained throughout the area and the chemistry may not reach completion before sundown (i.e., “the sun outruns the chemistry”). In this situation, VOC-limitation applies throughout the area, even to the peak O₃ concentrations, and thus mitigation will require VOC controls.

Mitigation of peak O₃ concentrations in urban areas is further confounded by three facts:

1. A given urban area can experience episodes characteristic of either scenario depending upon the specific conditions of that episode.
2. Biogenic emissions, if sufficiently large, can render VOC-based controls ineffective (see Section 3.4).
3. Long-range transport of O₃ and precursor species can limit the effectiveness of any locally based emission control strategy (see Section 3.5).

The development of tools to quantitatively and reliably assess the efficacy of VOC and NOₓ controls for the mitigation of peak O₃ concentrations — a major requirement of the policy maker - remains a major challenge for the scientist. Nevertheless some progress has been made in two classes of tools: Air Quality Modeling Systems (AQMS) (see Chapter 4) and observation-based methods (see Section 3.4). Moreover, it appears that a methodology for combining these tools in an air-quality management system can be developed (see Chapter 5).

### 3.2.3 Issue: What about the effects of NOₓ disbenefits?

**Finding:** Model simulations suggest that O₃ enhancements can occur from NOₓ emission reductions, but these enhancements are limited in spatial extent.

**Discussion:** The term “NOₓ disbenefits” refers to the phenomenon of fostering an increase in O₃ concentrations from a decrease in NOₓ emissions — an extreme example of VOC limitation. This phenomenon is clearly shown to occur within smog chamber experiments that simulate the formation of O₃ pollution in the laboratory. (A more detailed discussion of smog chamber experiments is presented in Section 3.3.6.) It has been argued that observations of higher O₃ concentrations on weekend days versus weekdays in some urban areas (e.g., Los Angeles, Toronto, Brussels) is indicative of the NOₓ disbenefit occurring in the real world as a result of changing mobile source emissions (Canadian – Data, 1997; Dumollin et al. 1999; Altschuler, et al., 1995).
As illustrated in Figure 3.8, model calculations also predict that this phenomenon can occur. The effect occurs because, at high NOx concentrations, OH-radical scavenging via (R9) inhibits O3 production. However, these same model calculations indicate this effect is short-lived and rapidly overwhelmed by the catalytic effect of NOx on O3 production. As a result the NOx disbenefit generally should be limited to a relatively small region in and near urban cores and other major source regions. Even if reduction of NOx leads to an O3 increase in a given urban core, it still should reduce O3 in the surrounding region where higher O3 concentrations typically are found.

3.2.4 Issue: Reactivity-based VOC controls - Does this approach have benefits?

Finding: Emission-control strategies that attempt to reduce the reactivity of VOC emissions (as opposed to the total mass of VOC emissions) can have practical application in air masses that are VOC-limited and have limited contributions from natural hydrocarbon emissions.

Discussion: Reactivity-based approaches typically target the VOC species that are most productive in terms of O3 production (see Textbox 3.4), and thus can have a greater effect on O3 concentrations per pound of VOC emission reduction than an overall VOC control strategy (Carter and Atkinson, 1987). There are, however, limitations inherent to this approach. For example, it is only effective when VOC limitation applies and where natural hydrocarbon emissions are not dominant. Also, the reactivity of specific VOCs can change from locale to locale and thus the specifics of the approach must be regionally tailored.

3.2.5 Issue: O3 production efficiency from NOx - How Many O3 for each NOx?

Findings: Recent field studies indicate that only about 2 to 3 O3 molecules are produced for each NOx molecule emitted over North America.

Discussion: The O3 production efficiency (OPE) is defined as the number of O3 molecules produced per NOx molecule emitted. This parameter is especially relevant for the development of regional O3-mitigation strategies since it provides a rough indication of the reduction in O3 that might be expected from a given reduction in regional NOx emissions. Moreover, because OPE can be estimated through direct measurements of ambient O3 and NOx species, it provides an empirical or observation-based check on O3-control strategies developed using grid-based, prognostic air-quality models.

Initial estimates of OPE in North America indicated values in the range of 7 to 10 molecules of O3 per NOx emitted (Trainer et al., 1993, 1995; Olszyna et al; 1994). These initial estimates used chemical measurements at rural sites to establish an empirical, linear relationship between concentrations of O3 and the products of NOx; the value of OPE was then determined on the basis of this linear relationship (see Figure 3.15).

Chin et al. (1994) argued that the above approach probably overestimated OPE because NOx is removed from the atmosphere by dry and wet deposition more rapidly than is O3. Using empirical relationships between O3 and CO and NOx, these authors estimated a lower limit for OPE of only 1.7.

More recently, other approaches have been undertaken to better constrain OPE. These have involved direct, airborne measurements within power plant and urban plumes (e.g., Ryerson et al., 1998), as well as regional analyses of rural O3 monitoring data (Kasibhatla et al., 1998). As illustrated in Figure 3.16, these recent studies yield OPE-values in the range of only about 1 to 3 molecules of O3 per molecule of NOx and thus suggest that NOx-based strategies designed to reduce regional O3 concentrations by a given amount will require larger emission reductions than previously estimated. These studies suggest also that NOx emissions from different sizes and types of power plants and other point sources may produce different OPEs. Although this implies some interesting possibilities with regard to ozone-pollution management options, confirmation by additional field studies is needed. Furthermore, the full implications for regulatory controls have not been determined nor have OPE predictions of air-quality models been compared to
Ensuring that the models accurately portray the OPE for NO\textsubscript{x} is clearly important for developing regional emission controls.

3.2.6 Issue: How robust are the chemical mechanisms used to describe and simulate the VOC-NO\textsubscript{x}-O\textsubscript{3} relationship in the atmosphere?

Finding: The chemical mechanisms used in air-quality models are based on detailed measurements of individual reaction-rate constants and semi-empirical information derived from smog-chamber experiments. Chamber experiments, however, do not fully reflect atmospheric conditions and may have experimental artifacts. Recent advances in field measurement capabilities (e.g., transient species and oxidized products) present the opportunity to improve understanding of chemical mechanisms and NO\textsubscript{x}-VOC-O\textsubscript{3} relationships through diagnostic analyses (e.g., comparisons of predicted and observed OPE, oxidized product distributions, and indicator species ratios; CR6, CR13).

3.4 VOC Reactivity – What is it?

The term “reactivity” has been applied in a variety of ways in the ozone-management context. One (and perhaps the simplest) use of the term is the so-called kinetic or OH\textsuperscript{+} reactivity which expresses the reactivity of VOC in terms of their rates of reaction with the OH radical. For example, consider ethene and its oxidation by OH\textsuperscript{+}:

$$\text{OH}^+ + \text{C}_2\text{H}_4 \rightarrow \text{products}$$

where $k_{\text{C}_2\text{H}_4}^{\text{OH}^+}$ is the second-order rate coefficient for the reaction. The OH\textsuperscript{+} reactivity of ethene is simply equated to the magnitude of $k_{\text{C}_2\text{H}_4}^{\text{OH}^+}$. In other cases, the OH\textsuperscript{+} reactivity is expressed in terms of a pseudo first-order rate coefficient

$$k_1 = k_{\text{C}_2\text{H}_4}^{\text{OH}^+} \times [\text{C}_2\text{H}_4]$$

represents the ethene concentration. The advantage of this second definition is that it accounts for the concentration of the VOC as well as its rate constant with OH\textsuperscript{+} (cf. Figure 3.19).

Another more complex, but also more powerful definition of the term “reactivity” is used to quantify the ozone-forming potential of a VOC (Carter and Atkinson, 1987). This type of reactivity attempts to account for the number of O\textsubscript{3} molecules that are produced from the oxidation of a given VOC (referred to as the mechanistic reactivity) as well as the OH\textsuperscript{+} or kinetic reactivity described above. In a sense we can think of this type of reactivity as a sensitivity coefficient; i.e.,

$$\frac{\partial O_3}{\partial x_i}$$

where $O_3$ is some measure of ozone amount after a specified reaction time and $x_i$ is some other measure of the amount of a specific precursor, i. Since (1) represents an incremental change in O\textsubscript{3} associated with an incremental change in $x_i$, it is also referred to as an “incremental reactivity”.

Application of incremental reactivity has meet with some success. For example, Carter (1995) has applied the concept by constraining NO\textsubscript{x}/VOC ratios to either maximize expression (1), thereby yielding the “Maximum Incremental Reactivity” (MIR), or to maximize peak ozone concentrations, yielding the “Maximum Ozone Reactivity” (MOR) (see Figure 3.14). Carter has also suggested further consolidation of specific reactivity values by dividing reactivities for individual species by counterpart reactivities of the total VOC mixture, resulting in “relative incremental reactivities.” Associated model simulations suggest that these techniques can produce reactivities that are less sensitive to mechanistic and kinetic uncertainties and environmental conditions (CR19).
**Figure 3.14** Incremental reactivities for ethene as a function of initial VOC and NO\textsubscript{x} concentrations computed using a box-model simulation of a typical urban VOC mixture. MIR and MOR loci are depicted, respectively, by the upper and lower dashed lines. After Hales et al. (1993).

**Figure 3.15** Measured O\textsubscript{3} concentrations as a function of measured concentrations of the products of NO\textsubscript{x} oxidation at four remote sites in Eastern North America. Linear regression of the Scotia data yields the equation O\textsubscript{3} = 35 ppb + 8.5 x (products of NO\textsubscript{x} oxidation) with an \textit{r}\textsuperscript{2} of 0.99. The slope of 8.5 has been interpreted as being roughly equivalent to the O\textsubscript{3} production efficiency (OPE). However, more recent studies suggest that the actual OPE is significantly smaller than this value (see Figure 3.16 and text). After Trainer, et al, (1993).
CHAPTER 3

Discussion: The development of chemical-reaction mechanisms for atmospheric constituents is essential for elucidating and simulating the chemistry leading to the formation of \( O_3 \) and other important secondary atmospheric pollutants. Thus, accurate predictions of the quantitative relationship between \( O_3 \) precursor emissions (VOC and NO\(_x\)) and \( O_3 \) depend strongly on the correct depiction of the elementary chemical-reaction steps describing the atmospheric oxidation cycle (see Textbox 3.3).

Chemical mechanisms used in air-quality simulation models generally are formulated to reproduce data from smog-chamber experiments (representative of the chemical composition of typical urban atmospheres) using consensus sets of laboratory chemical kinetic reaction-rate constant data (CR14, CR15). This process appears to produce chemical mechanisms that are reasonably robust in their representation of smog-chamber data. For example, comparisons between predictions using state-of-the-science mechanisms and smog-chamber data indicate errors in \( O_3 \) concentration predictions from these mechanisms of \(~30\%\) for moderate to high VOC/NO\(_x\) ratios (CR15).

However, comparisons between model predictions and smog-chamber data most likely underestimate the actual errors in these predictions. One confounding problem is the need to correct for experimental artifacts introduced by the chamber walls. For many categories of VOC (and especially aromatics, natural hydrocarbons, and higher molecular-weight oxygenated compounds) only a fraction of the atmospheric products are known (CR14). Consequently, chemical mechanisms may not represent the ultimate fate of a sizable fraction of the carbon emitted as VOC, which in turn could seriously impair the ability of chemical mechanisms to accurately portray a multiple-day \( O_3 \) episode. More importantly, smog-chamber experiments have not been performed and verified for the full suite of VOC and NO\(_x\) concentrations of relevance to \( O_3 \) pollution. Few data are available for the low VOC/NO\(_x\) ratios encountered in some urban areas and power plant plumes and for low VOC and NO\(_x\) concentrations found in non-urban settings. As a consequence, the application of these mechanisms to the atmosphere is based upon an extrapolation from the high concentration ranges of the smog chamber to ambient air conditions. The lack of smog-chamber data at low-NO\(_x\) conditions is of particular concern. As new policies are promulgated that force greater attention to \( O_3 \) pollution in rural, low NO\(_x\) environments (see Section 3.8), this gap will likely become increasingly critical.

Figure 3.16  Estimated \( O_3 \) production efficiencies, OPE, in \( O_3 \) molecules per NO\(_x\) emitted. Two sets of OPE estimates are presented: the solid lines and squares (■) indicate OPE-values as a function of plume air parcel age, as inferred by Ryerson et al. (1998) from airborne measurements within three coal-fired power plant plumes in the Nashville area on July 7, 1995 during the Nashville/Middle Tennessee Ozone Study; the vertical line and diamonds (●) labelled “Northeastern Average” is the range in OPE estimated by Kasibhatla et al. (1998) from the ratio of the average daily \( O_3 \) concentration increase recorded at rural \( O_3 \) monitoring sites in the northeastern United States during selected stagnation episodes in the summer of 1995 and the NO\(_x\) emission inventory for the region.

![Figure 3.16 Estimated O₃ production efficiencies, OPE, in O₃ molecules per NOₓ emitted. Two sets of OPE estimates are presented: the solid lines and squares (■) indicate OPE-values as a function of plume air parcel age, as inferred by Ryerson et al. (1998) from airborne measurements within three coal-fired power plant plumes in the Nashville area on July 7, 1995 during the Nashville/Middle Tennessee Ozone Study; the vertical line and diamonds (●) labelled “Northeastern Average” is the range in OPE estimated by Kasibhatla et al. (1998) from the ratio of the average daily O₃ concentration increase recorded at rural O₃ monitoring sites in the northeastern United States during selected stagnation episodes in the summer of 1995 and the NOₓ emission inventory for the region.](image-url)
Corroboration of model prediction with observation-based methods may provide one avenue for addressing the inherent uncertainties in chemical mechanisms (see Section 3.7). For example, advances in chemical instrumentation now make it possible to compare model-predicted and observed \( \text{O}_3 \) production efficiency over a variety of environmental conditions. These comparisons, if they become standard practice in model application and evaluation, could provide an additional layer of confidence for the \( \text{O}_3 \) precursor relationships predicted by models.

### 3.3 CHARACTERIZATION OF ANTHROPOGENIC EMISSIONS: How Do We Assess Progress?

Air-quality management depends inherently on the ability to characterize the relationship between emission sources and pollutant receptors. For primary pollutants like \( \text{Pb} \), \( \text{CO} \), or \( \text{SO}_2 \), this relationship is largely determined by source distribution and transport. However, for secondary pollutants like \( \text{O}_3 \), which are generated by chemical transformation processes, the source-receptor relationship is generally more complex.

In the case of \( \text{O}_3 \), photochemical AQMS have constituted the fundamental analytical tool for relating precursor emissions to \( \text{O}_3 \) concentration and thus have often driven the need for VOC and \( \text{NO}_x \) emission inventories. Estimating precursor emissions, including their spatial, temporal, and chemical nature, has proved to be a major challenge. After 20 years of effort, emission estimates continue to be one of the weakest links in the air-quality management process and a major source of uncertainty in the development of \( \text{O}_3 \) control strategies.

Anthropogenic VOC and \( \text{NO}_x \) emissions are typically distributed across three broad source categories: point, mobile, and area. These source categories are often subdivided further. The three NARSTO nations do not use a uniform set of source categories (see Figure 3.17), so that direct comparison of source sector distributions among the nations is difficult. Standardization of source categories and subdivisions among the nations would prove useful in the harmonization of emission inventories and facilitate the intercomparison of the relative source sector contributions between nations. A fourth category, biogenic emissions, can also represent a significant contribution to the total emission mass, depending upon location, spatial scale, and time. Biogenic emissions are discussed in Section 3.4.
3.3.1 Issue: What improvements have occurred in our understanding and estimation of mobile source emissions in the last decade?

Finding: Field studies, summarized in NRC (1991), indicate that mobile-source emissions had been underestimated by factors of two or greater for VOC. Despite continued study of mobile-source emissions since the NRC report, significant questions remain regarding the accuracy of emissions derived from mobile-source emission models. As a result, the use of inventories from mobile-source emission models introduces additional uncertainty into AQMS.

Discussion: There are more than 230 million vehicles on the road in North America; approximately 68% are passenger cars, 26% light-duty trucks, and 6% heavy-duty trucks and buses (CR21). Vehicle emissions fall into two general categories: exhaust or tailpipe emissions generated as a by-product of the combustion process, and evaporative emissions arising from the direct release of gasoline vapors. Evaporative emissions can be further classified into, for example, running losses associated with evaporation of gasoline during the operation of a motor vehicle, hot soak losses associated with evaporative emissions after the engine has been turned off and is cooling, and diurnal evaporative emissions that occur while an unused motor vehicle is subjected to rising and falling temperatures over the course of a day.

Models are typically used to describe the amount and distribution of mobile source emissions from these vehicles in a given location for various conditions, while other models describe driving patterns within given grid elements in a modeling domain. Roadside measurements indicate that roughly 10% of the vehicles are responsible for more than 50% of the on-road hydrocarbon and CO emissions (Lawson et al., 1990 and Zhang et al., 1995). A major challenge to mobile-source models is accounting for this highly skewed distribution of vehicle emissions.

In North America, analysts use two regulatory mobile-source emission models: EMFAC7 (used for California) and MOBILE (used for the rest of the United States, as well as in Mexico and Canada) (CR21). The models use data from laboratory tests on the exhaust and evaporative emissions from a subset of the total population of the motor vehicle fleet to estimate fleet-averaged, area-wide emissions. To replicate actual emissions, tests are carried out for each of the relevant portions of the driving cycle and then aggregated using appropriate weighting factors. Since the models do not provide specific temporal and spatial information, additional algorithms based, for example, on profiles for diurnal temperature, speed, vehicle miles traveled must be applied to enhance the spatial and temporal resolution of the emissions derived from the mobile-source emission models.

An analysis of the 1987 Southern California Air Quality Study (SCAQS) tunnel study showed that the then-current version of these mobile-source models significantly underpredicted mobile-source emissions of hydrocarbons and carbon monoxide under the measured conditions (Ingalls, et al., 1989 and Pierson, et al., 1990). These models have been revised since that time, and predicted magnitudes of mobile-sources have increased significantly. Table 3.3, for example, indicates that EMFAC7-estimated reactive organic gas (ROG) and CO emissions have increased by more than a factor of two since 1988, while NO_x emission estimates have increased by more than 85%. The worrisome aspect of this trend is the steady increase in the emission estimates with each new version or release of the models, with no indication of convergence on a central value as the models have evolved over time. Also disturbing is the fact that there are significant discrepancies between emissions predicted by different models. For example, Table 3.4 shows a comparison of MOBILE5a and EMFAC7F for a specific set of conditions where the MOBILE5a model consistently predicts higher emissions than EMFAC7. Similar discrepancies have been shown for evaporative emissions.

3.3.2 Issue: What do atmospheric measurements tell us about mobile-source emission inventories?

Finding: Tunnel studies and roadside measurements have served to highlight and expose the complexities in estimating mobile-source emissions (CR21). Specific advances have been made in characterizing
the major sources of uncertainty and in estimating mobile-source emissions, but the accuracy of mobile-source emission estimates at any given place and time remains poorly quantified.

Discussion:  As noted in the previous section, mobile-source emission models such as EMFAC7 and MOBILE are developed using data from laboratory tests on a subset of the total population of motor vehicles. Three approaches have been taken to determine if the emissions developed from these tests are representative of the emissions from an actual fleet of vehicles operating under actual driving conditions: 1) tunnel studies in which the aggregate emissions from motor vehicles operating within a tunnel are measured; 2) remote sensing in which the tailpipe (i.e., exhaust) emissions of individual motor vehicles are detected from the roadside; and 3) source apportionment methods in which ambient measurements are used to independently estimate motor-vehicle emissions (CR21; CR12). It should be noted that these approaches, in and of themselves, do not provide a definitive and comprehensive evaluation of mobile-source emission models. Tunnel measurements provide information on motor-vehicle emissions for only one set of driving conditions. Remote sensing measurements of tailpipe emissions only address exhaust emissions. Finally, while source apportionment methods do, in principle, consider emissions in the aggregate for an area, they can produce ambiguous results because of uncertainties in the measurements as well as key parameters needed to link ambient concentrations to emissions. Despite these limitations, these methods can provide very useful insights into the accuracy of aspects of mobile-source emission models. The discussion below summarizes the results of key studies carried out over the past decade using these methods.
Tunnel Studies: The 1987 SCAQS Tunnel Study led to a major reappraisal of mobile-source emission models and ultimately to significant increases in the emission rates predicted by these models (see for example Table 3.3). At the time, the reappraisal of the mobile-source emission models triggered by the 1987 SCAQS Tunnel Study was thought to represent a major advance in our ability to characterize motor-vehicular emissions. Unfortunately, subsequent tunnel studies suggest that mobile-source emission models remain unable to accurately predict emissions from a fleet at a specific place and time. For example, studies in the Tuscarora Mountain Tunnel in Pennsylvania and the Ft. McHenry Tunnel in Baltimore in 1992 suggested that the new version of MOBILE overpredicted VOC, NOx, and CO emissions (Pierson et al., 1995). Measurements in the Sepulveda Tunnel in Los Angeles in 1995 indicated that the newest version of EMFAC underpredicted CO by a factor of 1.5, overpredicted NOx by 1.7, and was in close agreement with VOC. A similar study in 1996 indicated that CO and VOC were underpredicted by factors of 1.5 and 1.8, respectively, and NOx was overpredicted by a factor of 1.3 (Gertler, et al. 1997).

Remote Sensing: This technique uses optical methods to remotely measure the amount of CO, VOC, and NOx in exhaust emissions from individual motor vehicles (Bishop et al. 1989; Guenther et al. 1995; Zhang et al. 1993, 1996; Stedman et al., 1997; CR21). In order to obtain data for motor vehicles under typical driving conditions, the measurements are usually made at frequently traveled roadways such as freeway entrances and exits. Among the many insights gained from remote sensing studies carried out over the past decade, perhaps the most important relates to the role of “high-emitters” in the overall mobile-source emission inventory. It has been found that a relatively small fraction of the total fleet of motor vehicles (i.e., the high-emitters) are generally responsible for a disproportionate share of the total mobile emissions in a given area. For example, Beaton et al. (1995) found that 7% of the vehicles operating in urban areas in California were responsible for more than 50% of the CO emissions and 10% were responsible for more than 50% of the VOC emissions. Understanding why some motor vehicles are high-emitters and how to accurately represent their emissions in mobile-source emission models represent two major challenges for the coming decade.

Source Apportionment Methods: These methods attempt to provide an alternate approach for assessing emission inventories on the basis of ambient concentration data (Henry et al., 1994; Yarwood et al., 1994; Fujita et al., 1997; CR12; CR21). For the most part, studies using source apportionment methods have suggested that mobile sources are responsible for a larger portion of the total VOC emissions than that predicted by emission inventories. This lack of agreement between source apportionment methods and emission inventories remains an unresolved issue.

### 3.3.3 Issue: What improvements have occurred in our understanding and estimation of stationary source emissions in the last decade?

<table>
<thead>
<tr>
<th>EMFAC Version</th>
<th>Release Date</th>
<th>ROG</th>
<th>CO</th>
<th>NOx</th>
</tr>
</thead>
<tbody>
<tr>
<td>7D</td>
<td>January 1988</td>
<td>360</td>
<td>3500</td>
<td>500</td>
</tr>
<tr>
<td>7E</td>
<td>July 1990</td>
<td>475</td>
<td>3700</td>
<td>580</td>
</tr>
<tr>
<td>7EP</td>
<td>December 1990</td>
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<tr>
<td>7ESCF</td>
<td>May 1992</td>
<td>520</td>
<td>4500</td>
<td>690</td>
</tr>
<tr>
<td>7ESCF2</td>
<td>November 1992</td>
<td>500</td>
<td>4000</td>
<td>600</td>
</tr>
<tr>
<td>7F</td>
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<td>700^a</td>
<td>6138^a</td>
<td>745^a</td>
</tr>
<tr>
<td>7 G</td>
<td>October 1996</td>
<td>749^a</td>
<td>8169^a</td>
<td>929^a</td>
</tr>
</tbody>
</table>

* Emission estimates for EMFAC7F and 7G are based on ARB estimated changes for summer ROG and NOx, and winter CO inventories.
Finding: Several improvements have occurred that advance our understanding of emissions from point and area sources. As a result of the Clean Air Act Amendments of 1990, all major U.S. electric utility power plants are required to use continuous emission monitoring systems (CEMS). These new measurement systems provide a rich source of data for use in emission inventory evaluation and compilation. In addition, the United States has conducted an Emissions Inventory Improvement Program (EIIP) which has identified a number of areas for improvement. However, there remains a great deal of uncertainty in estimating NOx and VOC emissions for many area source categories, relative to power plants and light-duty motor vehicles (e.g., CR22).

Discussion: Traditionally, stationary source emissions have been estimated by using activity level or fuel-use data in conjunction with emission and control factors. For point sources such as electric utilities, data from CEMS can provide significant opportunities to evaluate emissions models and assess their accuracy in estimating the total mass contributions by individual chemical species as a function of averaging time (yearly to hourly). For example, the use of measured hourly-averaged NOx emissions in place of inventory estimates should reduce the uncertainty related to emissions in the simulation of O3 by air quality models.

An analysis conducted to compare national and state emission totals for 1995 obtained from summing all boiler emissions from CEMS, to emissions for those same boilers computed using fuel consumption data and published emission factors, shows that average U.S. NOx emission rates are 20% lower when CEMS estimates are used than when fuel use data are used. (CR22) Average SO2 emission rates from CEMS are 3% higher than those using the fuel data. Considerable variability exists when comparisons are made at the state level (and even more at the individual boiler level).

Although measured data from the CEMS are generally considered to be superior to estimates made using emission factors, one-time source tests, mass balance calculations or other estimation methods, several concerns and possible sources of uncertainty in the measurements have surfaced. Some of the most important of these concerns are:

- Reference methods sometimes lead to overestimated flow rates, heat rates, and SO2 emissions.
- Missing data substitution leads to overestimated emissions.
- Data handling, software, and reporting errors can occur.
- CEMS may be less reliable at low emission concentrations or other extreme conditions.

For many other types of point sources, CEMS are not required and may not be feasible. For these sources, emissions are generally estimated using the more traditional methods or by individual stack

<table>
<thead>
<tr>
<th>Pollutant</th>
<th>Speed (miles/hr)</th>
<th># of Runs</th>
<th>MOBILE5a (g/mile)</th>
<th>EMFAC7F (g/mile)</th>
<th>Van Nuys (g/mile)</th>
<th>MOBILE5a EMFAC7F</th>
</tr>
</thead>
<tbody>
<tr>
<td>HC</td>
<td>36-45</td>
<td>18</td>
<td>2.02</td>
<td>1.21</td>
<td>2.52 (0.20)</td>
<td>1.67</td>
</tr>
<tr>
<td>HC</td>
<td>11-15</td>
<td>2</td>
<td>6.26</td>
<td>4.78</td>
<td>5.00 (1.12)</td>
<td>1.31</td>
</tr>
<tr>
<td>CO</td>
<td>36-45</td>
<td>17</td>
<td>21.3</td>
<td>9.59</td>
<td>20.9 (0.77)</td>
<td>2.22</td>
</tr>
<tr>
<td>CO</td>
<td>11-15</td>
<td>2</td>
<td>68.2</td>
<td>36.3</td>
<td>40.8 (3.3)</td>
<td>1.88</td>
</tr>
<tr>
<td>NOx</td>
<td>36-45</td>
<td>17</td>
<td>2.71</td>
<td>1.51</td>
<td>1.53 (0.06)</td>
<td>1.79</td>
</tr>
<tr>
<td>NOx</td>
<td>11-15</td>
<td>2</td>
<td>2.53</td>
<td>2.14</td>
<td>1.26 (0.11)</td>
<td>1.18</td>
</tr>
</tbody>
</table>

* Standard error is given in parentheses, using the number of runs as the sample size.
testing. In the United States, significant efforts to improve emission estimates for point sources have been made under the EIIP. These efforts include fostering information sharing and joint methodology development, as well as specific efforts focused on categories that comprise a large portion of the major point sources of O₃ precursor emissions. Despite the improvements that have been made, there remains a great deal of uncertainty in these estimates. It is difficult to quantify this uncertainty due, in part, to the difficulty of obtaining information on the techniques used in the development of the estimates. The implementation of the recommendations of the EIIP should help to reduce this uncertainty. In addition, the development of improved emission factors, which is not a part of the EIIP, is key.

NOₓ and VOC emissions from stationary area sources are even more difficult to accurately characterize. These are sources that are too small or dispersed to be treated as individual point sources. Even though the individual sources may be small, collectively they can represent a significant portion of the emissions, particularly VOC, in an area. Emissions from area sources are nearly always estimated using some type of indirect estimation procedure. Direct measurement of area source emissions is hardly ever practical because of technical and cost considerations. Calculation of area source emissions may be based on extrapolation from a sample set of sources, material balance, mathematical models, or emission factors applied to activity factors derived from government or industry reports. Emissions from these sources are believed to suffer from outdated emission factors and lack of knowledge of activity profiles, especially for short-term periods (CR22). Little quantitative information has been reported that would place bounds on the uncertainty for either NOₓ or VOC emissions in these categories. Anecdotally, however, a few cases where reconciliation of source contributions from ambient VOC concentrations and from direct emission estimates suggests that VOCs from surface coating releases and from solvent use are much less than their proportions in emission inventories (CR12).

In the United States, the EIIP is attempting to update and improve emissions estimation methodologies for many area source categories through coordination of experts in developing recommended “best practices.” The EIIP area source program predominantly addresses sources of VOCs. While the EIIP does not involve any new source testing or basic research, its benefits are mainly derived from exchange of data between states that are doing new research and those needing better methods.

3.3.4 Issue: What are the major limitations to projecting accurate emission estimates in the future?

Finding: Uncertainties in activity growth rates and emission factors as well as the degree of compliance with emission regulations and the effectiveness of emission controls all contribute to uncertainty in emission projections. The greatest degree of uncertainty is likely to be associated with the prediction of activity growth rates. (CR22)

Discussion: Policy makers are concerned with how O₃ concentrations, and more generally air quality, might change in the future, with and without additional emission controls. These projections require a forecast of future emissions for a hypothetical future O₃ episode, usually applying the meteorological conditions of an historical and well-characterized O₃ episode. The future-year inventory is based on emissions for a current or historical base-year and some estimate of the emission changes as a result of growth, new technology, products, and behavior (for example, less evaporative solvents), and planned control factors. Usually these projections are made for the point, area, and mobile-source sectors, while biogenic emissions are assumed to be constant.

- For point sources, either a growth factor is assigned based on increases in future production due to economic growth, or growth may be limited based on known capacity limitations and the planning cycle. Facility retirements/retrofits also may be considered.
- For area sources, a growth factor is usually utilized which is based on either economic growth or population growth.
- For mobile sources, growth is usually based on projected changes in vehicle miles

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traveled as well as projected improvements from replacement of vehicles in the fleet.

Subsequently, various control-strategy projections are made to assess the impact of alternative control techniques on future emissions. Control-strategy projections are estimates of future-year emissions that also include the expected impact of modified or additional control regulations. Because regulations are not always 100% effective and are not always fully implemented, less than full effectiveness is often considered.

Assessing the accuracy of these future emission projections is difficult, especially when these projections are based on predictions of future human behavior. For example, earlier attempts to predict future mobile-source emissions have been marred by significant under-predictions in the growth in vehicle-miles-traveled (CR21).

In addition, the quality of an emission projection is only as good as the base-year inventory upon which it is based. Several ways of improving the quality of emission projections are:

- Make forecasts readily available to interested parties.
- Explicitly state and analyze the impacts of the assumptions behind the forecasts.
- Use more detailed or specific activity forecasts for high-emission source categories.
- Study changes in source characteristics that might affect emission rates over time and incorporate ways of taking such changes into account in the projections.
- Improve emission inventories that form the base year for the projections.

3.3.5 Issue: What have been the major advancements in emission modeling? What are the benefits of these advancements?

Finding: Over the last decade, several comprehensive emission modeling systems have emerged that facilitate emission estimates by collecting various algorithms and sub-models together within a single consistent framework. These systems have made diagnostic analyses of emission data possible. Such analyses have provided the opportunity to uncover systematic biases associated with specific emission components. In addition they are more “user friendly” and thus available to a much larger community. This improvement should stimulate broader interaction between the model developers and users, and improve overall quality in the inventories.

Discussion: Estimates of hourly pollutant gas emissions for each grid cell in a modeling domain are required for all emission-based O₃ air-quality models. Such relevant gases include CO, NO, NO₂, and categories of VOC species. Depending upon the scope of the model, they may also include SO₂, and fine/coarse particulate matter. Deriving day-specific and hour-specific estimates of these emissions from a wide variety of data sources of quite variable quality and quantity is a multi-staged engineering task that must be performed for each air-quality model application. Typically such emissions are estimated both for a base case (current or recent historical time period) as well as a near-future case, to predict the impact of proposed emission-control programs. The development of comprehensive emission-modeling systems over the last decade has facilitated emission estimates by collecting the various algorithms and sub-models together within a single consistent framework.

Basic data for many emission processes are estimated on annual or seasonal bases for a county, as part of an emission inventory conducted at a national or state/provincial level. For use in air-quality models, these data must be “disaggregated” to the model’s resolution requirements, often 4 to 40 km in space and 1 hr in time. In the emission modeling process, meteorological data are used to aid this disaggregation for those emission components that vary with temperature, winds, or solar radiation. Examples of such components are evaporative emissions from mobile source engines and biogenic emissions from vegetation. Also, chemical aggregation of the many emitted organic compounds into the particular aggregated or lumped organic categories required by an air-quality model’s chemical mechanism must be performed during emission processing. This aggregation, known as
the speciation step, is mechanism-specific. Emissions also must be temporally disaggregated from annual emission-inventory estimates to seasonal, daily, and finally hourly values.

In the late 1980s the first emission-modeling systems emerged for urban-scale airshed models (Emissions Preprocessor System, EPS; Causley, 1990) and for regional-scale models (Flexible Regional Emissions Data System, FREDS, Modica et al., 1989), bringing together the various emission-processing pieces into one system. Emission estimation for air-quality models was thus vastly improved, yet diagnostic analysis capabilities were limited. Visualization of component emission fields at various processing stages, a useful diagnostic feature, was not an internal component of these systems. A second generation of emission-modeling systems emerged in the 1990s. Examples include the related systems: Geocoded Emissions Modeling and Projections System, GEMAP, (Radian, 1993), the Emissions Modeling System-95, EMS-95, (AG, 1995), and Models-3 Emissions Processing and Projection System, MEPPS, (Benjey et al., 1997). The EMS-95 system was recently applied in processing the emissions for the OTAG project (OTAG, 1997). These systems include statistical and GIS-based visualization capabilities within the emission-modeling framework to assist in the various steps of processing, including county-to-grid cell allocations, land-use and land-cover mapping, and diagnostic analysis/quality assurance. They also include emission projection modules, based upon economic growth projections. A similar, but more computationally efficient emission system has also come into recent use, the Sparse Matrix Operator Kernel Emissions (SMOKE) system (Houyoux, 1996; MCNC, 1999).

The emergence of these new capabilities in comprehensive emission modeling systems has opened up the earlier convoluted multistage emission processing approach to a larger community, including air-quality scientists. The effects of this evolution are yet to be fully appreciated, but it is clear that these systems are helping to move emission estimation from crude engineering practice to more of a scientific discipline. On the other hand, the existence of these modeling systems does not alter the fundamental gaps in understanding and the ability to quantify O3 precursor emissions. Furthermore, it should be borne in mind that attempts to deterministically quantify emissions on a given day

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**Figure 3.18** Relative Incremental Reactivity (RIR) of nitric oxide (NO), total hydrocarbons (THC), and the components of THC, anthropogenic hydrocarbons (AHC) and natural hydrocarbon (NHC) for the Atlanta Metropolitan Area during a summer day in 1990 as inferred using the Observation Based Model driven by measured concentrations of speciated hydrocarbons, NO, and O3. The bars indicate the percent reduction in O3 for each percent reduction in the respective precursor and the vertical lines above the bars indicate the standard error of the mean for percent reduction. Note the while the RIR for THC is ~ the RIR for NO, more than 50% of the RIR for THC is estimated to arise from NHC. (CR11).
3.4 BIOGENIC PRECURSORS: What is Their Role?

Biogenic precursors from natural sources are not generally controllable. An important policy perspective is to understand the distribution of biogenic emissions and how, where, and when they interact they interact with anthropogenic emissions, playing a role in the O₃ formation process.

The past decade has seen significant strides made in quantifying the sources of biogenic NOₓ as well as VOC and in documenting their role in O₃ formation in both the urban and rural environment. Nevertheless, substantial uncertainties (i.e., factors of 2 or 3) remain in estimates of the magnitude of biogenic VOC emissions. Reducing this uncertainty is critical to determining the relative effectiveness of controlling anthropogenic VOC and NOₓ emissions. Some key advances in our understanding of biogenic emissions are outlined below.

3.4.1 Issue: What is the role of biogenic VOC emissions in O₃ production?

Finding: Isoprene, a VOC that is a by-product of photosynthesis, is ubiquitous in much of the lower atmosphere over North America, and its participation in photochemical O₃ pollution has been confirmed by direct observation.

Discussion: In recent years, understanding of the role of biogenic isoprene (C₅H₈) in urban and rural oxidant formation has improved substantially. These research findings have supported the theory advanced in the late 1980s that isoprene plays a confounding role in the O₃ pollution problem by diminishing the effectiveness of VOC-based O₃ mitigation strategies (see for example, CR6, CR10 and CR11). Specifically:

- Isoprene concentrations, measured in urban as well as rural areas with significant biogenic VOC sources (e.g., the U.S. Southeast), indicate that isoprene is a major contributor to overall VOC reactivity in these areas (e.g., Figure 3.18).
- Atmospheric observations have qualitatively confirmed that spatial and temporal variations in isoprene are generally consistent with the patterns predicted by biogenic emission models (see Figure 3.19).
- Laboratory data have aided identification of isoprene oxidation by-products, helping to elucidate the chemical pathways for isoprene’s participation in photochemical-smog production (Carter, 1996 and CR14). Direct observations of atmospheric by-products of isoprene oxidation tend to confirm the existence of these chemical pathways (Montzka et al., 1993; Starn, et al., 1998). Other observations provide evidence of O₃ production in the atmosphere from air containing a mixture of isoprene and anthropogenic NOₓ (St. John et al., 1998).

3.4.2 Issue: What is the role of natural NOₓ sources?

Finding: Natural NOₓ sources, including lightning-produced NO and biogenic NOₓ emissions from unmanaged soils, are relatively small when compared to anthropogenic sources over North America.
Comparison of: A. Predicted isoprene emissions; and B. Observed isoprene levels in a 6-state area of the United States. Emissions were calculated using the BEIS2 emission algorithm for a day in July 1995. The isoprene concentrations were measured aboard the NOAA P-3 aircraft (between 1000 and 1600 hours and at altitudes below 1000 m) during the 1995 SOS Nashville/Middle Tennessee Ozone Study. Note the general consistency between those regions predicted by BEIS2 to have large isoprene emissions and those that were found to have large ambient isoprene concentrations. (CR10).

Figure 3.19
Nitrogenous fertilizer application can enhance soil emissions, but these emissions are considered to be anthropogenic, as opposed to “natural.”

Discussion: Current estimates indicate that the magnitude of natural NO\textsubscript{x} sources over much of North America is considerably smaller than anthropogenic sources and thus the contribution of natural NO\textsubscript{x} to the production of either rural or urban O\textsubscript{3} pollution over the continent is small (CR23). However, NO\textsubscript{x} emissions from soils can be enhanced considerably by the application of nitrogenous fertilizers. Model calculations suggest that fertilizer-induced soil emissions of NO\textsubscript{x} may make a highly variable, but non-negligible contribution to O\textsubscript{3} formation in rural areas with significant agricultural activity (e.g., San Joaquin Valley in California or areas in Illinois). These latter emissions, while biogenic, are caused by human activities and are thus not “natural.” Moreover, their impact on O\textsubscript{3} formation could, in principle, be reduced through manipulation of the form, timing, and method of application of nitrogenous fertilizers.

### 3.5 METEOROLOGICAL PROCESSES: Stagnation, Long-Range Transport, Or Both?

Policy makers are continually challenged by the confounding influence meteorological processes have over potential solutions to the ozone management problem. A clear understanding of the complex and varying meteorological processes is fundamental in evaluating their effect on ozone formation and transport and in designing effective control strategies. This section describes significant progress that has occurred in our scientific understanding of the local, regional, and synoptic atmospheric transport processes that govern ozone episodes. Equally important progress has taken place in our ability to model these processes and incorporate this knowledge in AQMS and OBM for effective control strategy design.

The horizontal and vertical distribution of O\textsubscript{3} and its precursors is critically dependent upon the dynamics of the planetary boundary layer (PBL; the lowest 1 to 2 km of the atmosphere) and the large-scale motions affecting regional transport. In recent years, significant advances have been made in our understanding of the interactions between the meteorological processes that lead to large-scale stagnation, which favor the accumulation of ground-level O\textsubscript{3}, and those that cause long-range transport of O\textsubscript{3} and its precursors.
3.5.1 Issue: What meteorological forces contribute to regional and urban air-pollution episodes?

Finding: A commonly occurring meteorological event leading to atmospheric conditions that are conducive to an air-pollution episode is the stagnation of a synoptic-scale (>1000 km) high-pressure system.

Discussion: High-pressure systems, and their associated large-scale stagnation, generally track slowly from west to east across North America. With weaker forcing in the warm-weather months, these large air masses can settle into place for days to a week or more. Weak winds, subsiding air from aloft, and strong inversions capping the PBL in the center regions of these systems lead to reduced ventilation near the surface and increased concentrations of pollutants near their sources. This can result in the appearance of numerous local or urban-scale O₃ pollution episodes embedded within a region of more amorphous, regionally dispersed O₃ concentrations (Figures 3.20 and 3.21).

During these periods of large-scale stagnation, locally induced meteorological processes can dominate and greatly exacerbate the severity of O₃ pollution episodes. For example, some of the worst air-pollution events in Atlanta have been found to occur under high-pressure stagnations, when local wind reversals move the urban plume back into the city each afternoon on consecutive days (St. John and Chameides, 1997). Similarly, some of the most severe air-quality problems occur in areas subject to land-sea effects, which restrict dilution and recirculate pollutants (e.g., Los Angeles, Chicago, New York, Houston) (see Figures 3.21 and 3.22) and/or in regions of complex topography that physically restrict ventilation (Mexico City, Los Angeles, Vancouver). Recent field studies (CR13), including the COAST study in the Houston/Galveston area (1993), LMOS in the Chicago/Lake Michigan basin (1991), LIFVOS in the Vancouver area (1993), and the SCAQS and SCOS studies in the Los Angeles/Southern California region (1987, 1997), have continued to examine these locally induced transport processes. Results of these studies generally have confirmed the importance of locally induced meteorological processes and have led to the application of spatially and temporally high-resolution monitoring and modeling. These include radar wind profilers (CR5), which provide time-frequent details of the vertical wind structures, and nested meteorological models (CR17), using assimilated radar, profiler and other data to better characterize local-scale meteorological regimes.

3.5.2 Issue: If stagnation fosters O₃ pollution, why is long-range transport of significance?

Finding: A variety of processes can trigger long-range transport of pollutants that have initially accumulated as a result of stagnation.

Discussion: Over time, plumes of varying scales within stagnant high-pressure systems can meander, merge, and circulate. Air pollutant patterns may be highly variable, with strong gradients between the stagnant portion of the system and its outer edges. As pollutant plumes move toward the outer edges of the high-pressure system, winds increase, plumes merge, and regional pollution patterns become more homogeneous. In these areas, pollutants that had effectively accumulated in the stagnating portion of the system can be transported by stronger winds aloft, bringing increased background pollutant levels hundreds of kilometers downwind and away from the center of the air mass.

Meteorological features at regional scales can also affect transport and dilution of pollutants. Channeled flows and low-level jets can affect transport in the 200-800 m layer above the ground. These phenomena can form in conjunction with synoptic-scale high-pressure systems. For example, Figure 3.23 presents a schematic of transport regimes observed during the NARSTO-Northeast field program in 1995 in the northeastern United States (Blumenthal et al., 1997). The channeled flows may transport pollutants from the southwest along the coastal urban “corridor,” although other directions (i.e., through gaps in the Appalachians) may also occur. Strong directed air flow confined to layers above the ground that form at night (i.e., nocturnal jets) also can lead to long-range transport (see Figure 3.24). In fact, during the 1995 NARSTO-Northeast field study low-level jets were observed on most nights preceding a regional high O₃ episode day.
Figure 3.20 The analysis of surface pressure (mb) and diurnal maximum O₃ concentration (ppb) for June 18, 1990. After Vukovich (1995). Many O₃ pollution episodes over eastern North America are associated with a strengthening of the Bermuda high pressure zone, while polluted cases over California are often associated with an eastward extension of the East Pacific ridge zone (CR17). This figure is illustrative of a regional O₃ pollution episode in eastern North America with a stagnating high pressure system over the south-central region and a stronger transport regime in the periphery of the system along the northeast Atlantic coast. The highest O₃ concentrations are seen roughly in the area of the central axis of the system, as well as in the transport area along the system’s periphery, which also coincides with a dense area of source emissions of O₃ precursors.

Figure 3.21 Transport vectors (relative magnitude) and 90th percentile of daily maximum O₃ concentrations over the eastern U.S. during the 1991-1995 O₃ seasons. The vectors were calculated from a Monte Carlo trajectory model using archived Nested Grid Model data. Vector length is a relative indication of transport magnitude for those days when O₃ concentrations were greater than the 90th percentile value over the multi-year period. (After Schichtel and Husar, 1998 and OTAG, 1997) Regional surface O₃ patterns are shown here because of their strong association with long-range transport of O₃ and oxidants, which are in turn governed by upper-level winds. These patterns are shaped, in part, by O₃ that has been brought to the surface from aloft by convective meteorological processes. Note that the flow regimes shown here represent transport winds in the lowest few kilometers above ground, the region traversed by the trajectories in the Monte Carlo model. A more complete illustration of transport depicting flows at upper and lower levels for the northeast United States is shown in Figure 3.23.
The conceptual understanding of meteorological processes interacting at large and small scales to affect local \( O_3 \) concentrations has evolved over time. Instead of reflecting a single spatial scale, peak concentrations have been found to arise from a complex and probably nonlinear interaction between \( O_3 \) formation occurring on all spatial scales as well as transport of \( O_3 \) and its precursors from one area to another and from one region to another. Further complications arise from the fact that the relative contributions from each scale and process can vary from one episode to another and from one region to another. For example, the conditions for long-range transport appear to be much less prevalent in the southeastern United States than in other portions of the eastern North American continent (see Figure 3.21).

The realization that interacting meteorological scales influence pollution phenomena has substantially changed the constraints on management practices in North America. Contributions to local peak \( O_3 \) concentrations attributable to processes arising from long-range transport suggest that geopolitical boundaries are unlikely to provide an effective framework for devising \( O_3 \) abatement strategies. Coordinated multi-state/multi-province actions, such as those of OTAG, as well as multinational decisions are likely to be needed.

### 3.5.3 Issue: Have meteorological simulation models improved their ability to describe the phenomena that are significant to air pollutant accumulation in the troposphere?

**Finding:** Advanced mesoscale (~200 to 2000 km) meteorological models, such as the Mesoscale Model-Version 5 (MM5), the Regional Atmospheric Modeling System (RAMS), and the compressible community model (MC2), represent the state of the science in meteorological simulation modeling on nested regional and urban scales (CR17 and Benoit

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**Figure 3.22** Schematic summary of the processes affecting the lake-breeze circulation cell and its transport over Lake Michigan. An east-west section through midlake is shown during gradient southwest wind flow over Lake Michigan. The complex circulation patterns over the lake and near-by land areas are associated with a mesoscale lake breeze regime that can lead to high \( O_3 \) concentrations near the shorelines and over the lake. In general, land/lake or land/sea breeze circulation regimes can foster sharp gradients in pollutant concentrations. For example, during the hot summers of 1987-1988 in the Lake Michigan basin north of Chicago, exceedances of the 120 ppb \( O_3 \) level were 4.5 times more likely at monitors within 20 km of the lake shore than at monitors farther inland (Lyons et al., 1995). Schematic from Lyons et al. (1995), courtesy of C.S. Keen, of Mankato State University.
**KEY FINDINGS IN THE SCIENCE OF OZONE POLLUTION**

**Figure 3.23** Schematic of three distinct transport regimes inferred from observations during the NARSTO-NE Experiment (June-August 1995). The darkest vectors represent the synoptic scale flow direction, generally west to east. However, on the lee side of the Appalachian Mountains a low-pressure trough formed that modified or channeled the flow to a southwesterly direction (medium vectors). The lightest wind vectors indicate daytime near-surface (up to 200 m) wind flows that were, in general, significantly affected by sea breeze regimes along the northeast U.S. coast. These channeled and near surface wind regimes have the potential to contribute to long-range transport of O$_3$ and its precursors along the Northeast corridor. (After Blumenhal et al., 1997)

**Figure 3.24** Evolution of a low-level nocturnal jet in New Jersey on the night of July 31-August 1, 1995, as observed by a radar wind profiler. Because these nocturnal jets are not in direct contact with the surface and occur at night, they can transport pollutants for 100s of kilometers. With sunrise and the breakup of the nocturnal inversion, the transported pollutants can be re-incorporated in the PBL where they can contribute to an air pollution episode in a locale far removed from their initial sources. After Ray et al., (1997).
et al., 1997), and are significant improvements on earlier diagnostic characterization methods. However, issues remain concerning the link between these models and the needs of air-quality modeling systems.

**Discussion:** Mesoscale meteorological models are now able to realistically simulate many atmospheric scales of motion of importance to air-quality modeling systems. However, they cannot capture all relevant scales. Also, boundary-layer and surface parameterizations in meteorological models have improved greatly in recent years, enabling better representation of the spatial and temporal evolution of mixing heights and consequently, dilution. Complex flows such as land/sea breezes and terrain-forced flows now can be represented in a dynamically consistent manner. This is a significant benefit to the air-quality analysis and modeling community, which has relied for many years on objective and diagnostic analyses of routinely measured surface and aloft meteorological data. In complex flow regimes the density of measurements inevitably are inadequate to capture the true texture in the meteorological fields. Models such as MM5, RAMS, and MC2 are able to provide a more realistic representation within these regimes.

The addition of four-dimensional data assimilation (4DDA) to advanced meteorological models (Stauffer and Seaman, 1994; CR17) combines the best features of the numerical models and meteorological measurements into one system. With 4DDA, routinely measured meteorological data and/or special field-study data help “nudge” the simulations toward observations and minimize error accumulation. Currently, advanced meteorological models that include 4DDA are being used for meteorological characterization in air-quality analysis in complex flow areas such as the San Joaquin Valley of California (Seaman and Stauffer, 1996; Seaman et al., 1995), Chicago/Lake Michigan (Lyons et al., 1995; Shafran et al., 2000), and the northeastern United States (Michelson and Seaman, 2000; Seaman and Michelson, 1998). One challenge posed by meteorological models utilizing 4DDA is the development of independent evaluation techniques. Since assimilating observations into the simulation generally improves the accuracy of model results, the tendency has been to include as many observational data as are available. However, this removes an independent source of data for evaluating the model. Studies that have withheld data for evaluation showed that the use of 4DDA in meteorological models improves simulation skill (e.g., Michelson and Seaman, 2000). The application of 4DDA can vary considerably between air quality studies; very few guidelines exist and some 4DDA techniques are highly experimental. Some factors that influence the 4DDA methodology include the types of data available, the scale and complexity of the meteorology represented by the simulation, and the interactions of the 4DDA with the model physics. In general for air quality, coarsely resolved regional simulations assimilate data that have already been analyzed into gridded meteorological fields, while more finely resolved urban/local simulations nudge the simulation toward individual observations. Although the last decade has seen a body of scientific literature evolve describing the applications of nudging techniques, they remain largely empirical.

Simulation of clouds and rainfall, especially the summertime convective type of cloud (cumulus and stratocumulus) continue to pose difficult problems to meteorological modelers. Fair-weather cumulus clouds embody important mechanisms for venting pollutants from the lower portions of the planetary boundary layer. Cloud simulations are also needed for computing aqueous phase chemical reactions, especially significant to acid deposition and fine particle chemical models. It is important also to simulate clouds in space and time for accurate modulation of the radiation input to photochemical O$_3$ models and biogenic source-emission models. Accurate cloud simulations are needed to improve the characterization of precipitation patterns, important for pollutants that are soluble or can be rained or washed out to land or water bodies. New data assimilation techniques using data from radar wind profilers and eventually from satellites (soil moisture, temperature, and cloud measurements), as well as improved treatment of surface-atmosphere interactions, hold promise for future improvements in these areas.

Another inherently weak area is the inability of mesoscale meteorological models to accurately simulate flows in stagnating, or weakly forced systems, conditions often associated with O$_3$.
episodes. In the center regions of such systems, winds and mixing heights can be more strongly influenced by local thermal and dynamic forcing than by synoptic-scale phenomena. Advanced meteorological models are capable of generally describing the large-scale features of a stagnating high-pressure system, but often have difficulties representing local thermal and dynamic forcing. This introduces a stochastic component to the model’s representation of the atmospheric state which can, in turn, produce modest directional errors in wind fields, with the potential for large errors in the estimation of plume trajectories. This limitation to the determinism of current state-of-the-science meteorological models is being explored with the use of “ensemble” predictions. Ensembles are formed from model runs using slight perturbations in initial conditions or somewhat different internal physics or numerics. The variation in model results among the ensemble runs represents the uncertainty in the prediction (CR17).

Adaptation of gridded fields from advanced meteorological models to air-quality model grids has raised some questions as to the adequacy of mass consistency (Byun, 1999). Care must be exercised when interpolating the meteorological data in time or space so that mass conservation errors do not enter the process and corrupt the data for use in chemical/air-quality models. (See Textbox 3.5). However, the move from diagnostic characterization of meteorological fields using simple interpolation techniques to advanced dynamical models has improved the consistency in the characterization of meteorological fields for air-quality analysis and modeling and enabled the modeling of complex flow situations in areas that lack a dense meteorological network.

### 3.6 MEASUREMENTS, INSTRUMENTATION, AND NETWORKS: What Can We Measure?

The identification and measurement of critical variables is essential for defining and understanding the state of the atmosphere and its change with time. In the North American nations, air-monitoring networks have performed reasonably well in characterizing urban air quality by tracking time changes in relevant pollutant concentrations. Since some pollutants (specifically \( O_3 \) and secondary PM), are formed through atmospheric reactions, it is necessary also to characterize the precursors that participate in their production. Routine high-quality measurements of speciated VOC and NO\(_x\) are critical to effective \( O_3 \) management. Such measurements can provide the foundation for effective air-quality management (as discussed in Chapter 5) and for improving our ability to evaluate control-strategy effectiveness and progress in attaining regulatory objectives and/or standards.

**Section 3.6 Measurement, Instrumentation, and Network Issues**

**POLICY RELEVANCE:** Routine, accurate ambient monitoring of \( O_3 \) and its precursors is imperative to the policy community for a number of practical reasons: designing effective management strategies; tracking progress in improved air quality as a result of implemented \( NO_x \) and/or VOC control strategies; and, evaluating human and ecosystem exposure to \( O_3 \). It is critical to understand whether existing networks are adequate to meet the needs of the policy-community, and, if not, what improvements can be realistically made in the near future.

- **3.6.1** What are the major scientific challenges in \( O_3 \)-related monitoring?
- **3.6.2** What is the role of network monitoring in air-quality management systems?
- **3.6.3** What improvements would make monitoring networks in North America more effective?
- **3.6.4** How can the development of advanced instrumentation by the research community help in understanding the processes that control the formation of \( O_3 \) and PM\(_{2.5}\) in the atmosphere?
3.5 The Move to Advanced Meteorological Models

Methods for characterizing meteorological fields for air-quality models have changed and improved rapidly over the last decade. Simple objective analysis techniques on observational data from meteorological networks now are being replaced by advanced numerical models based on the first principles of atmospheric dynamics and thermodynamics. This migration to advanced models has improved the meteorological characterization for air-quality analysis, but it has also created some potential pitfalls and hidden dangers for air-quality modelers. Earlier characterization methods as well as the first meteorological models relied upon the assumption that mass changes caused by air movements are locally in balance. This simplification, although not always valid, assured mass conservation and thus stable solutions to the complex equations used in air-quality models.

The most recent advanced meteorological models (the so-called “non-hydrostatic” models) do not assume local mass balance (CR17). A potential problem arises in utilizing these meteorological fields in an AQMS. With meteorological fields produced from the earlier models using simplifying assumptions, an AQMS could re-diagnose some components, such as the vertical wind velocity, to conform to the specific requirements of the AQMS grid structure and time resolution. This re-diagnosis was consistent with the original meteorological characterization, and further assured mass conservation required by the AQMS’ chemical reactions.

With fields produced from the newer meteorological models, it is inappropriate to re-diagnose the fields if consistency with the original characterization is to be assured. However, most of the newer meteorological models do not guarantee local mass conservation. Therefore the AQMS must adapt to the fields as they are. Generally, this does not pose a problem since most of the time the meteorological fields are locally well-behaved. However, where winds are rapidly accelerating or decelerating, the AQMS chemical solution may become unstable unless steps are taken to compensate for the mass inconsistencies. Air-quality modelers have attempted to deal with these inconsistencies in a variety of ways. Some models attempt to compensate for the effects of the mismatch by adjustments in the AQMS numerical solutions. This can sometimes lead to the adjustment term dominating the solution (see discussion on MM5-AQMS in Chapter 4). Another technique involves adjusting the original fields produced by the meteorological model before they are provided to the AQMS to assure mass consistency (Byun, 1999). However, any adjustment has the potential to upset the dynamic balance of the meteorological model solution and cause undesired and often unanticipated effects in the AQMS concentration estimates. Future developmental work in meteorological modeling for air-quality analysis should emphasize maintaining mass consistency among dynamic and thermodynamic variables and should endeavor to maintain local mass conservation. Also, advanced AQMS that use meteorological data from current models should be configured as close as possible to match the spatial and temporal resolutions of the meteorological model to minimize interpolations on the original data fields.

3.6.1 Issue: What are the major scientific challenges in O₃ related monitoring?

Finding: Monitoring networks are an essential part of any O₃ management strategy. Such networks have been established to meet one or more of the following objectives:

- Document exposure of human populations and sensitive ecosystems to O₃
- Develop information on processes controlling the formation and distribution of O₃ in order to develop effective management strategies
- Measure the degree of compliance with emission regulations and the effectiveness of emissions controls.

Each of these objectives places different demands upon the network in terms of species measured,
instrument sensitivity, and location. Each also introduces operational and analytical challenges with regard to instruments and personnel.

**Discussion:** At least two major issues arise as the monitoring research community attempts to deal with the conflicting network priorities and the analytical challenges of routine measurements:

- **Identifying the problem versus finding the solution: An unresolved conflict.** The current O$_3$-related observing systems consist primarily of O$_3$ monitors located in urban areas (see discussion in Section 3.1). While these networks were designed to document human exposure, they reveal little about the appropriate management strategies needed to mitigate high O$_3$ concentrations or the success of current emission-control strategies in producing the desired results (i.e., attribution of changes). To become more relevant to designing and tracking O$_3$-management strategies, these networks will need to place a greater emphasis on measuring O$_3$ precursors and provide broader spatial coverage, especially in suburban and rural areas. Because of the importance of horizontal transport and vertical mixing, greater attention to developing a sustained measurement capability aloft is needed.

- **Inability to measure the critical species in a regular monitoring mode.** Ozone monitoring in North America is typically performed using UV absorption. Under clean, dry atmospheric conditions, such monitors have been found to be accurate and robust, and can be operated routinely by support-level personnel. Under highly polluted conditions, however, aromatic VOCs and/or their reaction products have been found to interfere with and degrade the quality of UV-based O$_3$ measurements **(CR3)**. This suggests that UV absorption may not be the appropriate monitoring technique for all types of air-quality monitoring sites. In particular, it may be prudent to use an alternative technique (e.g. chemiluminescence) to monitor O$_3$ at locations that are directly impacted by significant sources of aromatic hydrocarbons.

  Ozone-precursor monitoring is even more difficult **(CR3)**. Gas-chromatographic techniques for VOC measurement require careful attention and highly skilled operators. Currently, quantification of VOCs and especially oxygenates is largely unreliable, except under the direction of skilled researchers. **[e.g. CR3]**. These problems are particularly acute for alkenes and the higher weight aromatic hydrocarbons. A formal field intercomparison of ambient VOC measurements is essential to understand and address these measurement problems **(CR3)**.

  Although continuous NO and NO$_2$ measurements are made routinely within the North American nations, the chemiluminescence instrumentation employed often lacks sensitivity for NO and specificity for NO$_2$ (see Figure 3.25). As a result, the NO$_2$ data being gathered at North American network sites are often inadequate for studies focused on understanding O$_3$-related processes, possibly leading to erroneous conclusions (see for example, Cardelino and Chameides, 1995). Moreover, despite documentation of shortcomings in specific NO$_x$ instrumentation (Fehsenfeld et al., 1990; Gregory et al., 1990) and the current availability of selective and sensitive instrumentation **(CR3)**, NO$_x$ measurements using outdated instrumentation continue to be made at monitoring sites throughout North America.

The research-measurement community **(CR3)** has demonstrated that many of the most important chemical species in the atmosphere can be measured with acceptable quality. However, if progress is to be made in the transfer of these research-measurement technologies to network-monitoring operations, more attention must be given to:

- Evaluation of the field worthiness of instruments under typical network operating conditions
- Identification of the skill level and training
requirements of the operating technicians
- Development of the technical and human infrastructure required to support calibration and quality assurance
- Development of the data reduction and analysis capacity for the timely assessment of data in terms of stated data quality objectives. Of course, the development of less costly high quality instruments would likely increase their usage and lead to a more reliable set of ambient measurements.

Most measurements of \(O_3\) precursors and even meteorological parameters are taken at the surface, with only limited measurements taken aloft. Additional measurements above the surface would provide valuable insights into \(O_3\) formation and distribution.

3.6.2 Issue: What is the role of network monitoring in air-quality management systems?

Finding: In addition to documenting the state of the environment in terms of pollutant standards/objectives and supporting the operation and evaluation of regulatory air-quality modeling systems, monitoring-network data can serve to drive the development and application of observation-based methods (see Section 3.7) and air-quality management tracking and feedback systems (see Section 3.8, Demerjian et al., 1995; and CR2).

Discussion: Historically, comprehensive precursor data sets were available only through special field-measurement programs. Precursor-monitoring networks, such as PAMS in the United States and the NAPS in Canada, are now coming on-line and could provide critical data needed to assist in control-strategy development and evaluation, emission tracking, trend analysis, and photochemical air-quality model evaluation. It remains to be demonstrated that all the stated needs can be served by these networks and that the measurement technologies deployed can meet expected data-

Figure 3.25 Comparison of simultaneous, side-by-side measurements of ambient nitrogen oxide species using the U.S. Federal Reference Method (FRM) and enhanced instrumentation made on August 5, 1996 in Yorkville, Georgia outside of the City of Atlanta. (This site is both a PAMS and an SOS/SCION monitoring site.) Because of the lack of sensitivity, the FRM at this site was unable to quantify NO and NO\(_x\) concentrations below ~ 8 ppb. Moreover, the FRM for NO\(_x\) is subject to interferences from other nitrogen oxide species and thus the measured concentrations for NO\(_x\) using the FRM at this site often approach that of NO\(_y\). Data obtained from the Georgia Department of Natural Resources and Dr. E. Edgerton.
quality objectives. As the community gains experience in using these data sets, the quality of the data should improve and a variety of analysis opportunities will develop that were previously impossible or impractical.

3.6.3 Issue: What improvements would make monitoring networks in North America more effective?

Finding: National networks need an enhanced appraisal process that provides comprehensive reviews of monitoring and data-quality objectives, as well as measures of the degree to which these objectives are being met. It is important also to assure that user-community needs are being satisfied. A feedback mechanism from the user communities to the monitoring community would be extremely beneficial in promoting the use, and improving the quality, of network data. In addition, adopting advanced technologies for data management and distribution and performing selective value-added analyses would facilitate timely and easy access of network data. This would also facilitate network harmonization as defined by the World Meteorological Organization (WMO).

Discussion: A systematic network appraisal process provides the opportunity to demonstrate the progress and success of measurement programs with regard to identified objectives and to justify long-term monitoring commitments. It also provides opportunities to address issues of spatial representativeness, effectiveness and potential redundancy in monitor deployment. Network performance evaluation and assessment, and the ability to report and correct network limitations should be an essential feature in all network designs. Harmonization of national networks across North America would provide added benefit; for example, to facilitate reconciliation of national air quality trends and transboundary issues.

The submission of air-quality data to a central archive, which then serves as the vehicle for its dissemination, can be cumbersome and inefficient. Real-time data processing and distribution is now technologically feasible for North America and has been demonstrated in meteorological networks world-wide, as well as in several local air-quality networks. Such access would stimulate the various user communities into exercising the data and thereby accelerate identification of potential problems in data-quality and siting issues. In addition, it would stimulate the development of diagnostic tools and analysis approaches that ultimately impact approaches to the air-quality management process itself. An example of how such a practice has led to significant operational and scientific advances is that related to the meteorological networks.

3.6.4 Issue: How can the development of advanced instrumentation enhance our understanding of the processes that control the formation of O₃ and fine particulate matter in the atmosphere?

Finding: Field-tested and evaluated state-of-the-science instrumentation provides the opportunity to compare observation and theory as well as provide the continuity to merge data across studies to characterize spatial gradients and analyze trend information.

Discussion: Significant advancements have been made in measuring a variety of atmospheric chemical species with adequate sensitivity to address many issues raised by the atmospheric chemistry and air-quality communities (CR3). Validated instrumental systems used in the measurement of NO, NO₂, NOₓ, CO, SO₂, speciated VOC, and O₃ have been performed by many research groups and may be viewed as reliable from a research perspective. Measurements of formaldehyde, alcohols, higher-order carbonyls, organic nitrates, peroxides, ammonia, sulfuric acid, and nitric acid have been performed by a smaller subset of the research community and must be viewed as more challenging, while the measurement of transient species (e.g. OH, HO₂, RO₂ and NO₃) must be viewed as being in a specialized research mode.

Recent intensive field-measurement programs (CR6, CR13) have shown that when the full complement of measurement systems is deployed in conjunction with selected meteorological measurements, significant progress in elucidating and extending the basic understanding of O₃ related chemical processes can be made. These intensive field studies require
3.7 OBSERVATION-BASED METHODS: A New Tool In The “Scientific Toolbox”

Three-dimensional, Eulerian AQMS provide, in mathematical language, an integrated and comprehensive statement of our current understanding of air-quality phenomena. As such, these models have become a key, if not central, tool in the development of O₃ abatement strategies for a given area or region. A detailed discussion of these models - their characteristics, advantages, and limitations - is presented in Chapter 4 of this report. Despite the considerable analytical power AQMS potentially offer to the policy maker, they also have drawbacks. As discussed in more detail in Chapter 4, a key limitation is the fact that AQMS are driven by highly uncertain emission inventories. In recognition of this limitation, scientists have developed a new category of analytic tools. These tools are the “observation-based methods” that use ambient air-quality observations as opposed to emission inventories to infer important relationships between O₃, its precursor compounds, and/or the sources of these precursor compounds. In this parlance, AQMS are referred to as “emission-based models” because emission inventories are used as input (see Figure 3.26). In this section, salient features of these new observation-based methods are reviewed.

3.7.1 Issue: What kinds of observation-based methods are available for evaluating emission-control options?

Finding: The scientific community has developed a variety of observation-based methods, ranging from those that rely solely on analysis of chemical measurements to more complex methods that rely on photochemical models as well as observations to diagnose VOC- or NOₓ-limitation.

Discussion: Observation-based approaches use high-quality ambient measurements of O₃, its precursors, and/or other secondary products of the photochemical smog mechanism to diagnose the underlying relationships between O₃ production and the sources of O₃ precursors in the area and at the time of the measurements. The most straightforward of these methods relies solely on air-quality data; for example, the determination of the O₃ production efficiency (OPE) from observations of O₃ and the oxidized products of NOₓ discussed in Section 3.2. More complex approaches use photochemical model simulations, and/or algorithms in tandem with air-quality observations, to evaluate the relative efficacy of VOC and NOₓ emission controls. In the discussion below, we focus on these more complex observation-based method.

Three observation-based methods that attempt to use air-quality observations to determine if O₃ production in an area is in the regime of VOC sensitivity, NOₓ sensitivity, or transition between the two limits, have been documented in the literature (CR8). The “Photochemical Indicator Method” (Sillman, 1995; CR7) uses observed ratios of specific chemical species, such as H₂O₂/HNO₃, to characterize the...
regime of precursor sensitivity. The MAPPER method uses ambient measurements in tandem with O₃-NOₓ relationships expected from smog-chamber experiments to derive the so-called “extent of reaction” (Johnson and Quigley, 1989; Blanchard et al., 1999; CR9). The “Observation-Based Model” (Cardelino and Chameides, 1995; CR11) uses air-quality observations to drive a photochemical box model that infers O₃ production sensitivity to precursors on the basis of Carter’s Relative Incremental Reactivity factors. These methods have been applied to evaluate conditions for O₃ formation in a variety of locations, including urban areas in the southeastern and northeastern United States (see Fig. 3.13), the California San Joaquin Valley and Los Angeles region (see Fig. 3.27), the Houston Gulf Coast area, the Lake Michigan region, and Switzerland and northern Italy. Evaluation of these results suggests a rough semi-quantitative equivalency between each of the parameters derived by the above methods (see for example, CR8). However, an intercomparison, involving an evaluation of results from each method for an identical set of conditions, has yet to be carried out.

Observation-based methods assess the sensitivity of O₃ to VOC and NOₓ in a given airmass using ambient measurements of specific atmospheric constituents instead of emission inventories. For this reason, they provide a way to evaluate the accuracy of more traditional model predictions and thus reduce the level of uncertainty associated with these predictions and improve the characterization of O₃ precursor relationships.

An operational drawback of observation-based methods is their reliance on measurements of the ambient concentrations of the relevant chemical

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**Figure 3.26** Schematic diagram illustrating how emission inventories and air-quality observations are used to help guide the development of an O₃ abatement strategy in the emission-based approach based on an AQMS (top panel) and an observation-based approach (bottom panel), respectively. An integrated approach that combines AQMS and observation-based methods in a decision-making process that stresses accountability is discussed in Chapter 5.
Figure 3.27  Relative sensitivity of $O_3$ to possible reductions in VOC and NOx emissions in the Los Angeles area on June 25, 1987 using the Measurement-Based Analysis of Preferences in Planned Emissions Reductions (MAPPER). The MAPPER results are derived from data collected at monitoring sites in the area during the South Coast Air Quality Study (SCAQS). The results for each site are represented as “clocks.” The triangles inside the clocks indicate, through shading, the extent to which VOC or NOx reductions will be beneficial in reducing $O_3$ concentrations at each site as a function of time, with VOC reductions being relatively more favorable in areas of light shading and NOx reductions in areas of darker shading. The size of the clock indicates the hourly averaged $O_3$ concentrations at each site. In this particular application, the MAPPER method displays a distribution of precursor sensitivities that is quite similar to that predicted by AQMS predictions for the area (see for example, Figure 3.12), thus providing observation-based corroboration for the emission-based method. After Blanchard et al. (1999).
constituents. In the absence of such data, observation-based methods cannot be used, and, if the data are inaccurate or incomplete, there is the potential for highly uncertain or even erroneous results (CR11). There is also the potential for misinterpretation when the observation-based method is not rigorously tested for sensitivity to uncertain assumptions. The morning VOC/NO\textsubscript{x} ratio is an example of an “observation-based method” that had been used fairly extensively in the 1970s and 1980s but is now recognized to give misleading results under some circumstances (Cardelino and Chameides, 1995).

3.7.2 Issue: Are observation-based methods intended to replace AQMS in the development of O\textsubscript{3} abatement strategies?

Finding: No, observation-based methods are best used to complement AQMS.

Discussion: As discussed above, observation-based methods provide procedures for deriving O\textsubscript{3} precursor relationships that are independent of emission inventories and other inherently uncertain inputs. However, these methods are not without their own limitations and uncertainties (see Table 3.5), and as a result are probably best used in conjunction with AQMS. In this capacity they can provide an observationally-based check on the predictions of AQMS and the associated abatement strategies. An air-quality management approach that combines AQMS and observation-based methods in a decision-making process that emphasizes accountability is discussed in Chapter 5.

3.8 NEW STANDARDS AND OBJECTIVES: Will They Affect Management Options?

Air-quality standards and objectives in North America are typically set by regulatory agencies on the basis of health-related studies (i.e., human exposure-chamber, epidemiological) and ecological effects studies. Effectively attaining these standards and objectives is, however, critically dependent upon our scientific understanding of air-quality phenomena and the tools used and developed by air-quality scientists to characterize and simulate these phenomena. In this section we address the scientific and policy-making challenges that will arise as a result of changes in the air-quality standards and objectives that are either being implemented or are being considered in the nations of North America.

3.8.1 Issue: What are the implications of O\textsubscript{3} standards and objectives, which are based on lower concentrations averaged over longer time periods?

Finding: The new O\textsubscript{3} standards and objectives recently promulgated in the United States and being considered in Canada likely will challenge regulatory approaches, scientific tools, monitoring networks, and make attainment more difficult.

Discussion: Health-related investigations and vegetative damage studies (Bascom et al., 1996a,b; Heck and Cowling, 1997; Canadian-Health, 1997; Canadian-Vegetation, 1997) point to deleterious impacts at O\textsubscript{3} exposure levels less than those of the...
O₃ standards and objectives that have characterized environmental policy in North America over the past decade. As a result, changes in the O₃ standard and objectives have occurred or are anticipated. In the United States, for example, a new NAAQS for O₃ has been promulgated; this new standard is based on an 8-hr average O₃ concentration of 0.08 ppm instead of the former 1-hr-0.12 ppm concentration. Adjustments of the air-quality objective in Canada are currently under review (Canadian - Summary, 1997). Insights from air-quality science suggest that implementation of new O₃ air-quality standards and goals based on a lower concentration, averaged over a longer time period, will have a significant impact on the abatement process. Specifically, these new standards and goals are likely to be:

- **More difficult to attain:** Retrospective analysis of O₃ data from the United States indicate that there will be many more exceedances of the new 8-hr NAAQS than of the old 1-hr standard (see Figure 3.28). Other analyses show a larger downward trend in 1-hr-averaged peak O₃ concentrations than in 8-hr averages (Lefohn, 1998).
- **Require far greater emphasis on rural/regional O₃ pollution:** Analysis of data from a limited number of truly rural O₃ monitoring sites in the eastern United States suggests that air-quality standards such as that being promulgated in the United States will result in widespread non-attainment in rural areas (see Figure 3.29). This in turn will require a further departure from the local emission-control approach to O₃ attainment that characterized much of the O₃ abatement process over the past two decades (see Section 3.3) and the development of region-wide management structures such as that of OTAG (see Chapter 2).
- **Enhance the need for O₃ and precursor monitoring sites in rural areas:** The current monitoring networks in North America were established with a distinct health-oriented standard, and given previous understanding of the nature of O₃ effects on health, these were largely urban in character. With the new O₃ air-quality standards and goals, considerably more extensive measurements of O₃ and O₃ concentrations in rural areas will be needed. Research on how to meet this need in a technically robust but cost-effective manner has yet to be completed.
- **Challenge AQMS:** For the most part, the evaluation of AQMS performance has focused on hourly-averaged concentration predictions in urban areas. Evaluation of AQMS performance vis-a-vis longer time-averaging periods (e.g., 8-hr) and in low NOₓ environments (see Section 3.2) needs more testing.

### Table 3.5 Observation-Based Methods: The Pros and Cons

<table>
<thead>
<tr>
<th>Advantages of Observation-Based Methods</th>
<th>Disadvantages of Observation-Based Methods</th>
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<tbody>
<tr>
<td>1. Uses actual concentrations of chemical species to define O₃ precursor relationships.</td>
<td>1. Requires extensive air-quality data, for species that are often difficult to measure.</td>
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<tr>
<td>2. Can determine VOC- or NOₓ sensitivity without relying on emission inventories.</td>
<td>2. Results critically dependent upon the spatial and temporal representativeness of the data.</td>
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<tr>
<td>3. Analyses are not computationally intensive so can be carried out for all episodes for which data exist.</td>
<td>3. Cannot forecast (i.e., project emission reductions needed to reach attainment). See Textbox 3.6.</td>
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<tr>
<td>4. Like AQMS, methods generally rely on data derived from smog chambers.</td>
<td>5. Cannot distinguish between O₃ produced locally, transported O₃ and O₃ produced from transported precursors.</td>
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3.6 Observation-Based Methods vs. AQMS: Diagnosis vs. Prognosis

Much of the difference in approach between the observation-based method to deduce \( \text{O}_3 \) precursor relationships and the method involving the application of an AQMS is related to the difference between diagnosis and prognosis. Diagnosis is the process of determining the current state of a system on the basis of available data. For example, a medical doctor can determine the nature of a disease on the basis of a physical examination. Prognosis is the act of making a forecast of how a given system will evolve from its current state to some future state.

The observation-based method adopts the diagnostic approach. It uses observational data to "diagnose" the current chemical state of the atmosphere. Because it is diagnostic and not prognostic, it does not predict the future state of the atmosphere; e.g., the peak \( \text{O}_3 \) concentration that would result from a given reduction in pollutant emissions. The AQMS, on the other hand, is intended as a prognostic tool and thus can be used to make predictions.

Both methods have inherent uncertainty. Some of the sources of uncertainty are common to the two methods (e.g., chemical mechanisms are often similar or the same). Other sources of uncertainty apply only to one method, for example the AQMS is affected by emission uncertainty while the OBM depends on the specificity and accuracy of air-quality data. Because they are influenced by different uncertainties they offer semi-independent and complementary methods to infer \( \text{O}_3 \) precursor relationships.

Figure 3.28 Scatterplot of daily maximum 1-hr \( \text{O}_3 \) concentration (\( C_{\text{max } 1-hr} \)) and daily maximum 8-hr \( \text{O}_3 \) concentration (\( C_{\text{max } 8-hr} \)) observed in the Atlanta Metropolitan Area from 1987 to 1993. Black squares indicate daily maxima for days that did not exceed either the former 1-hr-120-ppb U.S. NAAQS or the new 8-hr-80-ppb standard; blue squares are for days with an exceedance of the 1-hr-120-ppb standard but not the 8-hr-80-ppb standard; green squares are for days with an exceedance of the 8-hr-80-ppb standard but not the 1-hr-120-ppb standard; and red squares are for days with exceedances of both standards. A high degree of correlation between the two \( \text{O}_3 \) metrics was found \((r^2 = 0.92)\) with a linear regression slope of 0.744 and intercept of 5.3 ppb. Over the time period, there were 98 exceedances of the old 1-hr-120-ppb NAAQS; all but one of these also corresponded to an exceedance of the new 8-hr-80-ppb NAAQS. However, there were over 200 days when \( \text{O}_3 \) exceeded the 8-hr-80-ppb standard but did not exceed the 1-hr-120-ppbv standard. After St. John and Chameides (1997).
Figure 3.29 Rural $O_3$ monitoring sites in the eastern United States found to be in attainment (open triangles) and non-attainment (closed triangles) for: Top Panel - the 1-hr-120-ppbv U.S. NAAQS; and Bottom Panel - the 8-hr-80-ppbv U.S. NAAQS. After Saylor et al. (1998).
3.8.2 Issue: Can integrated abatement strategies be developed that simultaneously address $O_3$ and other air-quality problems?

Finding: $O_3$ and other primary and secondary pollutants are related through a complex web of common emissions and precursors, common photochemical production pathways, and meteorological processes. In principle, integrated, multi-pollutant abatement strategies are possible; however, in some cases (e.g., $O_3$ and $PM_{2.5}$) more research is needed before such strategies can be implemented with scientific and technical confidence.

Discussion: Because of the linkages between $O_3$ and other pollutants, it should be possible, and probably desirable, to develop integrated abatement strategies that effectively address other air quality problems, while at the same mitigating $O_3$ pollution.

Enhance the need to account for the natural-background $O_3$ concentration: In the final analysis, an air-pollution mitigation program can hope only to reduce the controllable (i.e., human-induced) component of the problem. As air-quality standards and goals are adjusted to lower $O_3$ concentrations, they come closer to what might be deemed the irreducible background concentration. Thus, assessment of the magnitudes of the reducible and irreducible components of the ground-level $O_3$ pollution problem becomes more critical (Lefohn, 1997a, 1997b). Unfortunately, characterization of the background $O_3$ concentration over North America is problematic because of the likelihood that anthropogenic emissions have already perturbed free tropospheric $O_3$ over much of the Northern Hemisphere (see Textbox 3.7).

3.7 Can we define a continental background $O_3$ concentration for North America?

Discerning a continental background $O_3$ concentration for North America is made difficult by the sparseness of $O_3$ data in remote locations of the continent (see Section 1.1) and the inherent variability in $O_3$ concentrations at any given location. If we assume that the background surface $O_3$ concentration for the continent is indicated by the minimum daytime surface $O_3$ concentrations observed at locations not directly influenced by urban and other anthropogenic influences, then the summertime average value is about 30-40 ppb although even in very remote locations of the Northern Hemisphere (e.g., U.S. national parks in North Dakota and Wyoming), 8-hr averaged $O_3$ concentrations of 60 ppb or more do occur on occasion (Lefohn, 1998). However, these are unusual events and are not considered representative of average continental-background conditions.

Moreover, when we speak of a so-called background concentration, we usually think of this level as representing some "natural" or irreducible concentration that is independent of anthropogenic influence. In the case of $O_3$ in the Northern Hemisphere, however, this appears to not be the case. As discussed in Chapter 1, retrospective analysis of eighteenth century data from Europe suggests that $O_3$ concentrations in the Northern Hemisphere may have doubled over the past century in response to the massive industrialization that has taken place. If this is the case, then it is likely that the 30-40 ppb continental background alluded to above is in fact due in part to the anthropogenic emissions of $O_3$ precursors from our continent and thus significant reductions in $O_3$ precursor emissions over North America could lower the apparent continental background $O_3$ concentration as well as urban and regional $O_3$ concentrations. Because $O_3$ production on the regional and continental scale is NO$_x$-limited (see Section 3.2), reductions in NO$_x$ emissions would likely have the greatest impact on the continental background.

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e The couplings between $O_3$ and other pollutants also makes it possible for policy-makers to use the same basic emission inventories, air quality modeling systems, and sampling networks to develop mitigation strategies and track their effectiveness.
example, many if not most, of the air quality problems we face in North America are closely tied to our use of fossil fuels. A reduction in our reliance on these fuels would undoubtedly improve air quality on many fronts including that related to \( \text{O}_3 \).

More targeted multiple-pollutant abatement strategies are possible when the interrelationships between pollutants are well understood. For example, \( \text{NO}_x \) is a precursor for acid rain as well as \( \text{O}_3 \), and thus reductions in \( \text{NO}_x \) can help alleviate \( \text{O}_3 \) pollution as well as acid deposition.

**Figure 3.30** Flow diagram illustrating four possible responses to a regional decreases in power plant \( \text{NO}_x \) emissions. Heavy solid arrow is the intended effect of the emission control, the solid arrow represent likely side effects of the emission control, and the dashed arrow represents more speculative side effects. The center channel illustrates the intended effect of such an action: namely, a reduction in \( \text{O}_3 \). Moreover, since the oxidation of \( \text{NO}_x \) leads to the formation of \( \text{HNO}_3 \), we might expect that a reduction in \( \text{NO}_x \) emissions would also reduce nitrate-containing particle concentrations and hence \( \text{PM}_{2.5} \) in general (i.e., the far-left channel in the figure). However, nitrate particle formation is often controlled by the availability of gaseous \( \text{NH}_3 \) rather than \( \text{HNO}_3 \) and thus, a reduction in \( \text{NO}_x \) emissions may have no effect on particulate nitrate. On the other hand, if the reduction in power plant \( \text{NO}_x \) emissions is accomplished via selective non-catalytic reduction (SNCR), a process that requires the addition of \( \text{NH}_3 \) to the effluent stream, it will likely increase power plant emissions of \( \text{NH}_3 \) (NAPAP, 1990). The net result could be an increase in \( \text{NH}_3 \text{NO}_3 \) formation and an increase in nitrate-containing particles instead of a decrease (i.e., the right-central channel in the figure). Since both \( \text{O}_3 \) and sulfate formation are triggered by atmospheric oxidation and \( \text{O}_3 \) itself is the atmosphere’s most abundant photochemical oxidant, we might expect that a \( \text{NO}_x \) strategy that reduces \( \text{O}_3 \) concentrations might also reduce \( \text{PM}_{2.5} \) (i.e., the left-central channel in the figure). On the other hand, the rate of \( \text{SO}_2 \) oxidation and sulfate formation can be dominated by in-cloud oxidation and this process can be limited by the \( \text{H}_2\text{O}_2 \) abundance (Chameides, 1984; Hegg, 1985). Moreover, a reduction in \( \text{NO}_x \) can lead to an increase in \( \text{H}_2\text{O}_2 \) (Kleinman, 1991), and thus the possibility exists that a reduction in \( \text{NO}_x \) could lead to an increase in sulfate-particle formation (i.e., the far-right channel in the figure). Note, although this diagram presents positive and negative benefits resulting from \( \text{NO}_x \) reductions, the measurable magnitude of such impacts, if any, is unknown.
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When the interrelationships between pollutants are not well understood, more caution needs to be exercised before an integrated strategy is implemented. O₃ and PM₂.₅ appear to fall within this category. As illustrated in Figure 1.5, these two pollutants are coupled by common emissions, precursors, and photochemical pathways. It is not surprising therefore, that episodes of high O₃ often coincide with PM₂.₅ episodes, especially in the summer and in the eastern portion of the continent. However, because of the complexity of the mechanisms that couple these two pollutants, there does not appear to be a simple relationship between O₃ and PM₂.₅ and a given control strategy aimed at one pollutant has the potential to help or hinder the abatement of the other pollutant. For example, consider the range of possible responses to hypothetical decreases in NOₓ and VOC emissions illustrated in Figures 3.30 and 3.31. In both cases, the ultimate effect of a given control strategy on O₃ and PM₂.₅ will depend upon the relative strengths of the various coupling mechanisms. At the present

![Figure 3.31](image-url)  
**Figure 3.31** Flow diagram illustrates possible responses to a decrease in VOC emissions. Heavy solid arrow is the intended effect of the emission control, the solid arrow represent likely side effects of the emission control, and the dashed arrow represents more speculative side effects. In addition to the direct effect of decreasing PM₂.₅ organic concentrations (the central channel in the figure), a reduction in VOC emissions could have the beneficial effect of reducing O₃ (the left-hand channel in the figure) and the disbenefit of indirectly leading to enhanced HNO₃ and PM₂.₅ nitrate concentrations by reducing the formation of PAN (the right-hand channel (Meng et al.,1997). Note, although this diagram presents positive and negative benefits resulting from VOC reductions, the measurable magnitude of such impacts, if any, is unknown.
time, our understanding of these mechanisms is incomplete and thus we cannot yet reliably predict what the combined PM$_{2.5}$/O$_3$ response in a given region will be to a specific pollution abatement measure. The development of a more complete understanding of the PM$_{2.5}$/O$_3$ system will require focused, process-oriented field studies (e.g., CR24).

Even such seemingly distinct environmental problems as O$_3$ pollution and global climate warming are related and can therefore be addressed through an integrated abatement strategy provided our understanding of the relevant processes is sufficiently robust. For example, when present in the upper troposphere, O$_3$ is a very effective greenhouse gas (IPCC, 1995). Strategies that reduce O$_3$ concentrations on urban and regional scales without increasing the export of O$_3$ precursor compounds to the free troposphere might limit O$_3$'s role in global warming while also mitigating O$_3$ pollution. However, reductions in tropospheric O$_3$ would also reduce concentrations of the free radical OH, which triggers the removal of methane (CH$_4$), another greenhouse gas. Thus the same strategy that mitigates O$_3$ pollution while also limiting O$_3$'s role as a greenhouse gas, tends to enhance global warming from CH$_4$. Fortunately, recent assessments suggest that the benefit from reducing tropospheric O$_3$ outweighs the disbenefit from increasing CH$_4$ (IPCC, 1995), and thus O$_3$ pollution mitigation likely also aids in limiting society's contribution to the greenhouse effect and global warming. A very different situation arises in the case of PM$_{2.5}$, since a decrease in PM$_{2.5}$ would likely decrease the cooling effect of atmospheric aerosols and further contribute to global warming (Charlson et al., 1990). Similar concerns have been raised with regard to the reduction in SO$_2$ emissions to alleviate acid rain from the deposition of sulfuric acid since SO$_2$ is also a precursor to sulfate aerosols (Wigley, 1991).