

# CHAPTER 1

## *INTRODUCTION: A New Continental Perspective on an Old and Vexing Problem*

The North American continent is a vast industrialized landmass governed by three sovereign nations with distinct cultures. The atmosphere that blankets Canada, the United States, and Mexico, however, is a common resource and its protection is a shared responsibility. Ground-level ozone ( $O_3$ ) is an atmospheric pollutant (see Textbox 1.1 and Figure 1.1) that poses a pervasive air-quality problem throughout the continent. Its detrimental effects on human health and ecosystems (cf. Federal Working Group, 1999; U.S. EPA, 1996; DDF, 1997) disregard national borders and its management has proven to be complex. What are the processes that cause elevated concentrations of ground-level  $O_3$  in North America? How can our understanding of these processes be used most effectively to manage and

reduce the adverse effects of tropospheric  $O_3$ ? These are the questions that form the focus of this report.

Commissioned by NARSTO,<sup>a</sup> this state-of-science assessment provides a unique tri-national perspective on the ground-level  $O_3$  issue. Its goals are to document scientific efforts to explain how  $O_3$  is formed and transported, as well as to describe policies intended to control and mitigate damage. Its intent is to build upon knowledge and past success to improve management of  $O_3$  pollution across the continent. Because scientists and policy makers are partners in the effort to successfully balance industrial progress and environmental protection, this document is intended to serve both groups as an audience.



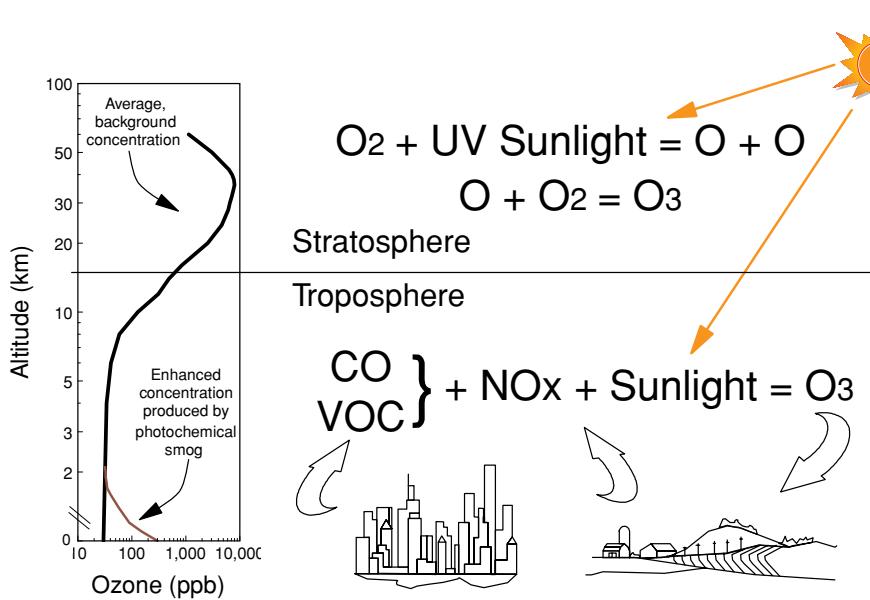
### 1.1 The Tropospheric Ozone Pollution Problem

Despite its seemingly minute concentration, atmospheric  $O_3$  has an enormous environmental impact. In the stratosphere, where about 90% of the atmosphere's  $O_3$  resides, it protects life from harmful ultraviolet radiation. In the troposphere,  $O_3$  is a key part of an oxidizing system that cleanses the atmosphere of a wide range of pollutants. At ground level, however,  $O_3$  can damage human health, agricultural yields, and other ecosystems.

Ground-level  $O_3$  abundances in non-urban regions of North America typically range from 20 to 70 ppb<sup>a</sup> (LeFohn et al., 1998). Hourly averaged values in excess of 100 ppb can occur, however, during regional or non-urban air pollution episodes. Peak  $O_3$  levels during urban air-pollution episodes tend to be substantially higher, with peak hourly-averaged values often exceeding 100 ppb and sometimes exceeding 200 ppb. The highest hourly-averaged  $O_3$  mixing ratio on record in North America is 680 ppb, measured in downtown Los Angeles in 1955. When  $O_3$  concentrations reach these levels, they impair lung function in humans and other animals and inflict foliar damage to agricultural crops, forests, and other vegetation (e.g., reducing yields and net primary production ).

<sup>a</sup>Throughout this report we refer to  $O_3$  abundances in terms of "mixing ratios," where 1 ppb  $O_3$  signifies a ratio of 1 molecule of  $O_3$  to every billion molecules of air and 1 ppm a ratio of 1 molecule of  $O_3$  to every million molecules of air.

<sup>a</sup>Formerly an acronym for "North American Research Strategy for Tropospheric Ozone," the term NARSTO has become simply a wordmark signifying a tri-national, public/private partnership for dealing with multiple features of tropospheric pollution, including  $O_3$  and suspended particulate matter. Additional information on NARSTO is available on <http://www.cgenv.com/Narsto>.



**Figure 1.1** Atmospheric ozone ( $O_3$ ). At left: The mixing ratio of atmospheric  $O_3$  as a function of height. At right: Photochemical processes responsible for producing  $O_3$  in the stratosphere and troposphere (including at ground level).  $VOC$  = volatile organic compound;  $NO_x = NO + NO_2$  = nitrogen oxide;  $UV$  = ultraviolet.

## 1.1 THE MOTIVATION - Why a Scientific Assessment Now?

This NARSTO assessment represents one in a sequence of assessments of ground-level  $O_3$  pollution in North America spanning more than two decades. The current assessment has been undertaken for important reasons:

- The problem persists.
- New and emerging air-quality policies create a need for scientific input.
- New scientific findings have implications for policy.
- There is a need for a continental perspective on ozone management.

### 1.1.1 The Problem Persists

Emission controls to mitigate  $O_3$  pollution began to be implemented in the United States and Canada in the 1970s and in Mexico in the 1980s (see Textbox 1.2 and Chapter 2). Trends in  $O_3$  concentrations at various urban locales in North America over the past decade suggest that these controls have produced beneficial results. For example, in the United States,  $O_3$  concentrations have generally been headed downward (Figure 1.3). Of

special note are the trends illustrated in Figure 1.4. These indicate that, *despite major growth in population and economic activity*, peak  $O_3$  concentrations declined significantly in Los Angeles (where  $O_3$  pollution has historically been the most severe in North America) and have been relatively constant in other particularly high-impact areas such as Houston and Mexico City.

However, the problem of ground-level  $O_3$  pollution in North America is far from solved. In 1995, it is estimated that some 70 million U.S. citizens, over 13 million Canadians, and 20 million Mexicans lived in or near areas where  $O_3$  concentrations violated  $O_3$  exceedance levels (U.S. EPA, 1996b; Canadian-Summary, 1997; SEMARNAP 1997). Moreover, 27 of 29 urban areas required by the U.S. Clean Air Act Amendments of 1990 to submit State Implementation Plans (SIPs) were unable to meet the 1994 deadline (see Section 2.2.4.1) because of the difficulties associated with developing a workable plan to reach attainment. The persistence of the  $O_3$  pollution problem in the face of concerted, sustained, and often costly efforts to address it has raised a perplexing question for both the scientific and policy-making communities: *To what extent does our inability to mitigate  $O_3$  pollution in North America reflect an inadequate scientific understanding of the underlying*

*causes of the phenomenon, a faulty application of this understanding, and/or simply the inability of society to control the socioeconomic drivers of O<sub>3</sub> pollution? (see Textbox 1.3).* Addressing this question has proven to be difficult, in large part because of a lack of sufficient monitoring over the past two decades. One way of approaching this issue would be to integrate an iterative tracking system into O<sub>3</sub> management programs (see Chapter 5).

### 1.1.2 New and Emerging O<sub>3</sub> and Particulate Policies Create Need for Scientific Input

#### 1.1.2.1 Revised Ambient O<sub>3</sub> Standards and Goals

Recent medical studies have uncovered statistically significant relationships between adverse health effects in humans (e.g., as measured by hospital admissions) and ambient O<sub>3</sub> mixing ratios well below 100 ppb (see, for example, Canadian-Summary, 1997 and the U.S. EPA, 1996a, and the references cited therein). These studies have precipitated a major reappraisal of the air-quality goals, standards, and policies of the North American nations related to O<sub>3</sub>. In the United States, the NAAQS has been lowered from a 1-hr, 0.12-ppm standard to an 8-hr, 0.08-ppm standard.<sup>b,c</sup> In Canada, an assessment designed to develop a new O<sub>3</sub> objective is currently underway.

While a critical review of the underlying health-effects data driving these new policies is beyond the scope of this assessment, the implications of these policies to the atmosphere are highly relevant. Our understanding of tropospheric O<sub>3</sub> suggests that attainment of these new goals and standards will not be a trivial matter and will require significant changes in the methods and approaches used to meet them. For example, as O<sub>3</sub> goals and standards are shifted to lower concentrations, it is likely that control strategies

will have to further emphasize the already emerging focus on regional, or even continental emissions (see Section 3.8).

#### 1.1.2.2 New Ambient Standards and Goals for Fine Particles

The fine-particle category commonly referred to as PM<sub>2.5</sub> includes atmospheric particulate matter with aerodynamic diameters less than 2.5 μm.<sup>d</sup> Because of their small size, such particles can penetrate into the deep lungs of a respiring individual and cause respiratory and other health effects. Recent epidemiological studies (NRC, 1998) have been interpreted to indicate a statistical association between adverse health effects and relatively low concentrations of PM<sub>2.5</sub>. As a result, a new NAAQS for PM<sub>2.5</sub> has been promulgated in the United States (Federal Register, 1997). The U.S. NAAQS for PM<sub>10</sub>, defined as particles with aerodynamic diameters less than 10 μm, remains in effect. In Canada, a scientific review and evaluation of atmospheric particulate matter was undertaken in 1997. New health-based air-quality objectives have been recommended for PM<sub>2.5</sub> as well as PM<sub>10</sub>.

As is the case for O<sub>3</sub>, a critical assessment of epidemiological data on the health effects of particulate matter is beyond the scope of this report. However, the technical issues surrounding the mitigation of O<sub>3</sub> pollution and PM<sub>2.5</sub> are interdependent. O<sub>3</sub> and PM<sub>2.5</sub> are coupled through common photochemical pathways and common precursors, as shown in Figure 1.5 and have similar dependencies upon meteorology during the warm months. Thus, control strategies designed to address one pollutant can affect the other. As discussed in Section 3.8, a major challenge for the coming decades will be to develop control strategies that take advantage of these interdependencies.

<sup>b</sup>The NAAQS are stated in units of ppm and to two significant figures. Thus, an exceedance is technically defined as a concentration of at least 0.125 and 0.085 ppm, respectively; i.e., concentrations that when rounded to two significant figures yield values equal to or greater than 0.13 and 0.9 ppm.).

<sup>c</sup>At the time this report was written, these revised standards were the subject of ongoing litigation. Regardless of the outcome of this litigation, the development and promulgation of these standards form part of the historical context in which this report was developed.

<sup>d</sup>The regulatory definition of PM<sub>2.5</sub> is “particles that behave aerodynamically as if they had diameters of 2.5 μm or less.”

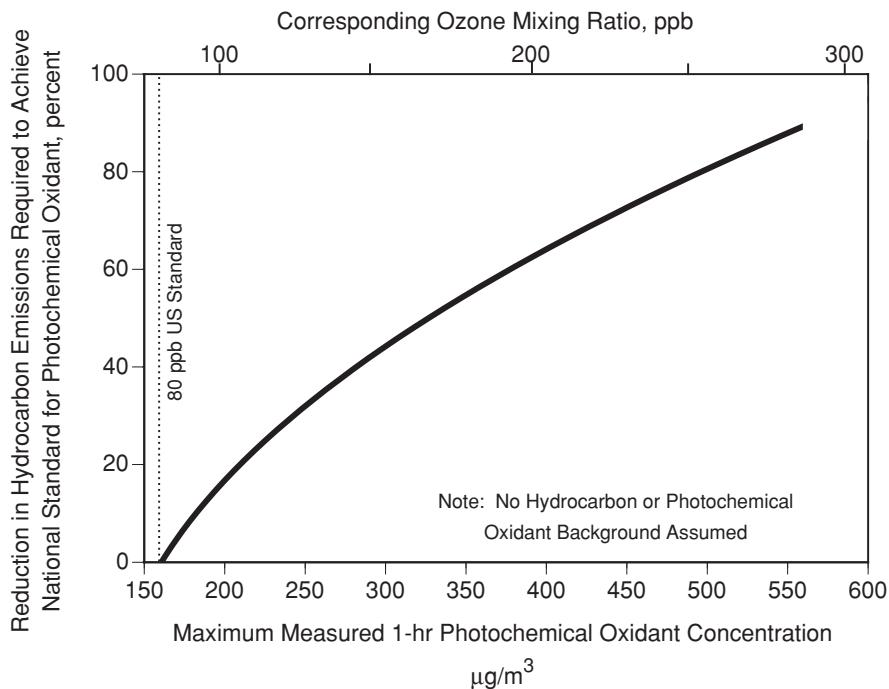


## 1.2 Historical Background

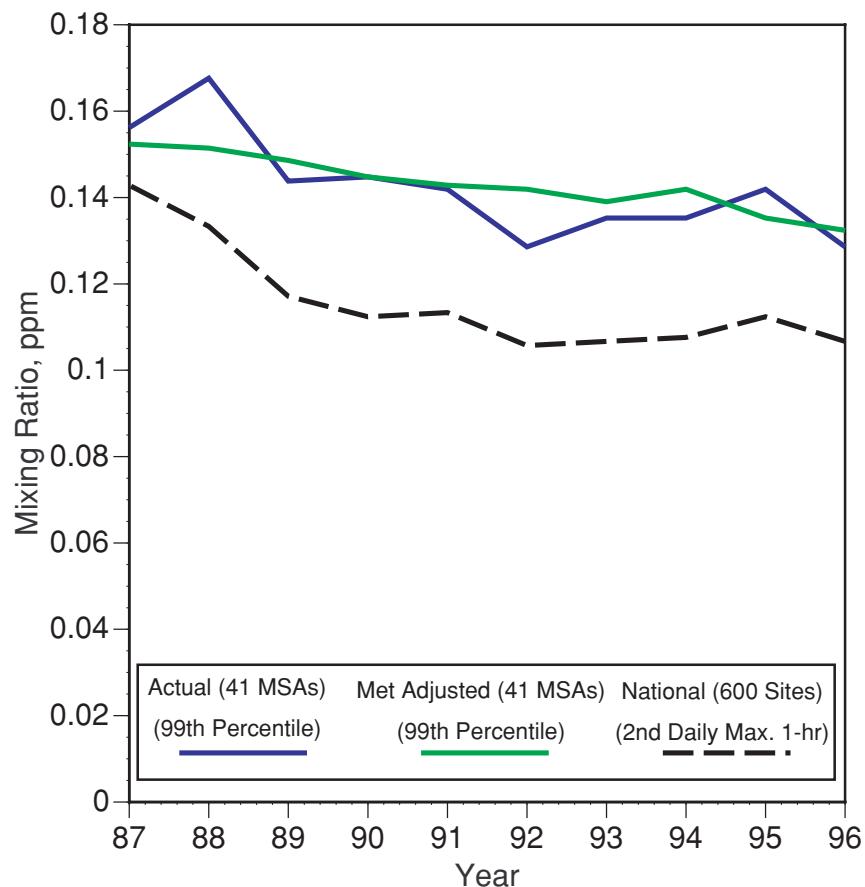
By the early 1960s, the contributors to O<sub>3</sub> pollution appeared to have been identified (as shown in the timeline of Table 1.1). Ground-level O<sub>3</sub> pollution is produced by the oxidation of VOCs in the presence of sunlight and NO<sub>x</sub>, as shown in Figure 1.1. VOC is derived from motor vehicle exhaust, evaporation of commercial and industrial solvents, and fugitive emissions from industry, while NO<sub>x</sub> is emitted as a by-product of combustion in motor vehicles, power plants, and other stationary sources. In the presence of these sources and under the appropriate meteorological conditions (i.e., high temperatures, low wind speeds), photochemical reactions quickly generate the large O<sub>3</sub> concentrations typically observed during urban O<sub>3</sub> pollution episodes. Control of ground-level O<sub>3</sub> pollution in an urban area can thus be accomplished, in principle, by simply reducing the local emissions of VOC and/or NO<sub>x</sub>. With this base of scientific understanding, and medical and epidemiological studies documenting the adverse health effects of O<sub>3</sub>, the stage was set for the promulgation of policies designed to address the problem. The United States, through the Clean Air Act of 1970, was the first of the three nations of North America to adopt a national air-quality goal for O<sub>3</sub> (referred to in the United States as a National Ambient Air Quality Standard or NAAQS) and a federally coordinated program to reach attainment of this goal within specific deadlines. Soon after, Canada and Mexico implemented their own control policies. On the basis of relatively primitive analyses of smog chamber and air-quality data, it was concluded that reductions in urban VOC emissions would provide the most effective strategy for reducing O<sub>3</sub>, and, as a result, initial O<sub>3</sub> abatement strategies tended to focus on the implementation of *local* VOC emission controls complemented by nationwide controls on automotive emissions of NO<sub>x</sub> as well as VOC (see Figure 1.2).

**Table 1.1** The Birth of Science of O<sub>3</sub> Pollution and Its Control

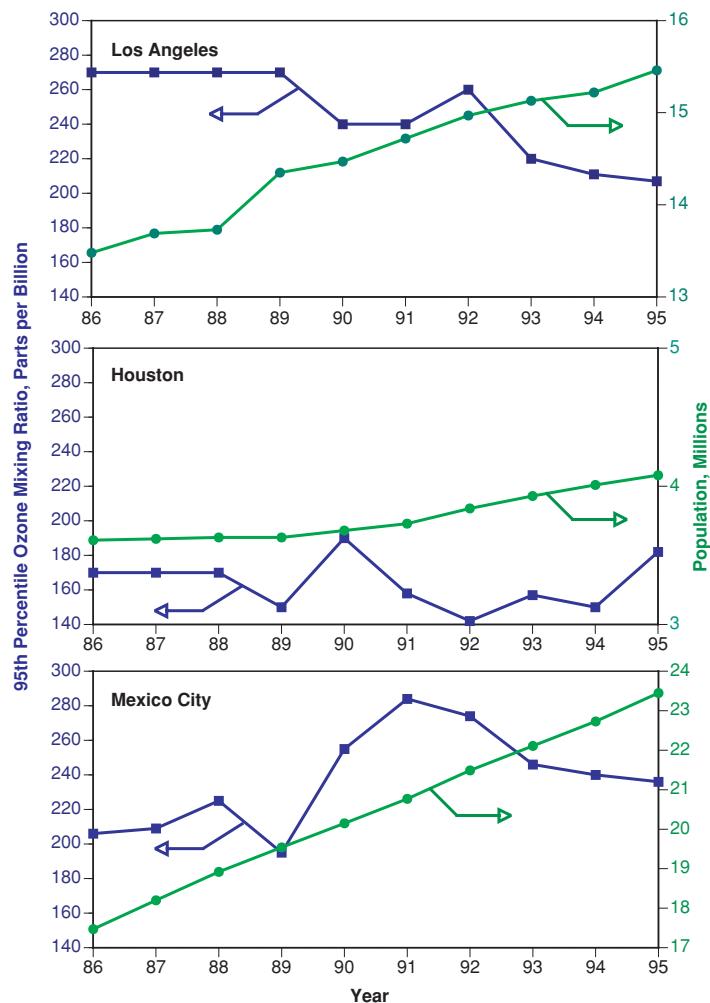
| Year        | Milestone   | Notes                         |
|-------------|---|-------------------------------|
| 1840s - 50s | O <sub>3</sub> molecule discovered<br>O <sub>3</sub> presence in atmosphere documented  | Schoenbein<br>(1840a&b, 1854) |
| 1874        | O <sub>3</sub> shown to be toxic to animals   | Andrews (1874)                |
| 1940s       | Photochemical smog found to be causing crop damage  | Middleton (1950)              |
| 1950s       | O <sub>3</sub> found to be major oxidant in photochemical smog<br>VOC and NO <sub>x</sub> shown to be O <sub>3</sub> photochemical precursors | Haagen-Smit (1952)            |
| 1961        | Basic science of O <sub>3</sub> pollution documented in monograph   | Leighton (1961)               |
| 1970        | U.S. Clean Air Act of 1970 establishes first national program for the mitigation of O <sub>3</sub> pollution in North America                 |                               |
| 1971        | Canada establishes O <sub>3</sub> air-quality objective   |                               |
| 1970s -80s  | Initial O <sub>3</sub> mitigation strategies tend to emphasize local VOC controls   | see Figure 1.2                |



**Figure 1.2** Initial guidance from the U.S. EPA on the required reduction in hydrocarbon emissions needed to achieve the NAAQS for photochemical oxidants (at that time of 80 ppb or  $160 \mu\text{g m}^{-3}$ ) as a function of the measured peak photochemical oxidant concentration. Current scientific understanding suggests that a significantly more complex situation often applies that will likely require a combination of VOC and  $\text{NO}_x$  controls (see Section 3.2) Source: Federal Register, V. 36, No. 158, 1971.



**Figure 1.3** Actual and meteorologically adjusted composite average  $\text{O}_3$  trends at 41 U.S. Metropolitan Statistical Areas (MSAs) and 600 urban, suburban, and rural sites. After U.S. EPA, 1997.



**Figure 1.4** Trends in annual 95<sup>th</sup> percentile daily O<sub>3</sub> maxima (blue) and population (green) at Los Angeles (top), Houston (middle), and Mexico City (bottom). O<sub>3</sub> data obtained from the U.S. Aerometric Information Retrieval System (AIRS) ([URL http://capita.wustl.edu/otag/DATA/AIRS\\_Data.HTML](http://capita.wustl.edu/otag/DATA/AIRS_Data.HTML)) for Los Angeles and Houston and from SEMARNAP (1997) for Mexico City. Population data were obtained from standard census sources and reflect populations in the Metropolitan Statistical Area of each city.<sup>e</sup>

### 1.1.3 New Scientific Findings Have Policy Implications

Scientists continue to significantly improve their understanding of the complex phenomena that cause O<sub>3</sub> pollution. For this improved understanding to be implemented, the conceptual framework and tools used by the policy maker in addressing O<sub>3</sub> abatement must also evolve. Improved communication and technology transfer at this science-policy interface are critically important to informed air-quality management decisions. New scientific insights into the complexity of the O<sub>3</sub>

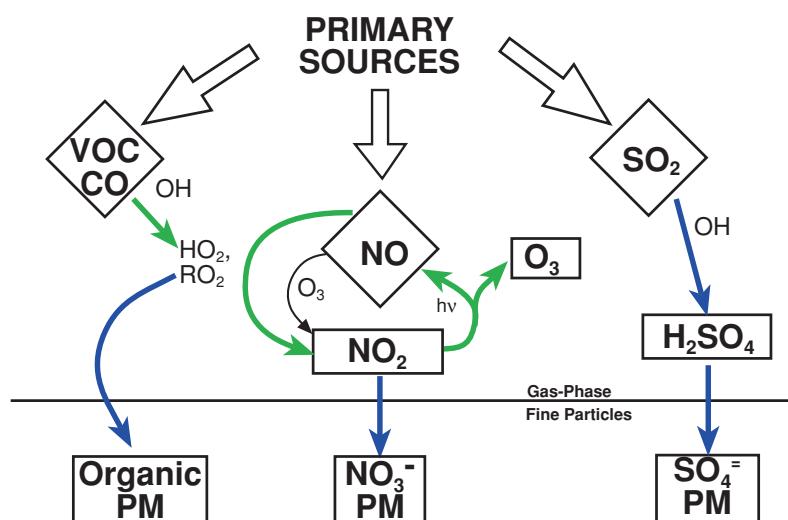
pollution phenomenon already have begun to spark significant changes in the policies adopted for managing O<sub>3</sub> pollution in North America; in turn, these have placed new burdens upon the scientific and technical communities. Key aspects of this changing science/policy landscape relate to O<sub>3</sub> trends, VOC and NO<sub>x</sub> emission controls, emission inventories, biogenic precursors, meteorological processes, measurement technologies and networks, new observation-based methods, and the implications of new air-quality standards and objectives. These aspects are discussed in Chapter 3.

<sup>e</sup>These urban population increases may be compared with national population growth rates between 1900 and 2000 as follows: Canada -- 27.8M - 31.3M (12.6%); U.S. -- 250.0M - 275.6M (10.2%); Mexico -- 84.5M - 100.4M (18.8%).

### 1.3 The Role of Science in Addressing the Ozone Pollution Problem

As with most environmental problems, ***scientific understanding is an essential but not the sole determinant*** in the mitigation of ground-level  $O_3$  pollution. Other factors related to technology, economics, and societal priorities can be equally if not more critical. Indeed, in the final analysis our scientific understanding of  $O_3$  pollution is already adequate to alleviate the problem. It is virtually certain that ground-level  $O_3$  pollution is caused by photochemical reactions involving the oxidation of VOC and CO in the presence of  $NO_x$  (see Textbox 1.1), and thus, in principle, society's contribution to ground-level  $O_3$  could be eliminated by ceasing all anthropogenic emissions of VOC, CO, and  $NO_x$ . For obvious reasons, such a solution to the  $O_3$  pollution problem is not currently a viable option. Society has instead opted to attempt to bring  $O_3$  concentrations down to acceptable levels of risk (i.e., levels that minimize adverse effects on human health and welfare) without unduly disrupting the technological infrastructure that underpins our economy and unprecedented standard of living. As a result, the scientific community has been given a much more difficult task than simply elucidating the causes of the pollution. It must identify the mix of VOC, CO, and  $NO_x$  emission reductions that will be most effective in lowering  $O_3$  concentrations and determine the minimum amount of emission reductions necessary to meet a given  $O_3$  air quality standard or objective. Actual mitigation of  $O_3$  pollution then requires the conversion of this scientific understanding into actual emission reductions through the promulgation of rules and regulations on specific types of emissions and the development and implementation of emission control technologies to comply with these rules and regulations. Economic and demographic projections also play a critical role, since economic and/or population growth can offset the emission reductions achieved through the application of an emission control technology. Efforts to mitigate  $O_3$  pollution can be hampered by a breakdown in any component of this process.

### Oxidant Production and Fine Particle Production



**Figure 1.5** Schematic illustrating coupling between the sources of primary gaseous pollutants (diamonds), the photochemical processes leading to production of  $O_3$  (green arrows) and those leading to the formation of fine particulate matter containing organics, nitrates, and sulfates (blue arrows).

## CHAPTER 1

### 1.1.4 Need for Continental Perspective in Policy Making

#### 1.1.4.1 *The Regional Perspective*

In the 1960s, photochemical smog was perceived as a basically urban problem. As a result of this perception, measures to address O<sub>3</sub> pollution focused mainly on local or urban-scale emissions. For example, in the United States, a two-level approach has been adopted: 1) nationwide controls on mobile and certain other sources; and 2) controls implemented on local, usually urban, scales. Determination of the final mix of controls implemented to reach the U.S. NAAQS has been in the past, and remains today, the responsibility of state and local authorities within a given non-attainment area. Similarly, design and implementation of measures to reach the ambient air quality objective in Canada and Mexico are a shared responsibility of the federal, provincial and local governments, comparable to the two-level system in the United States.

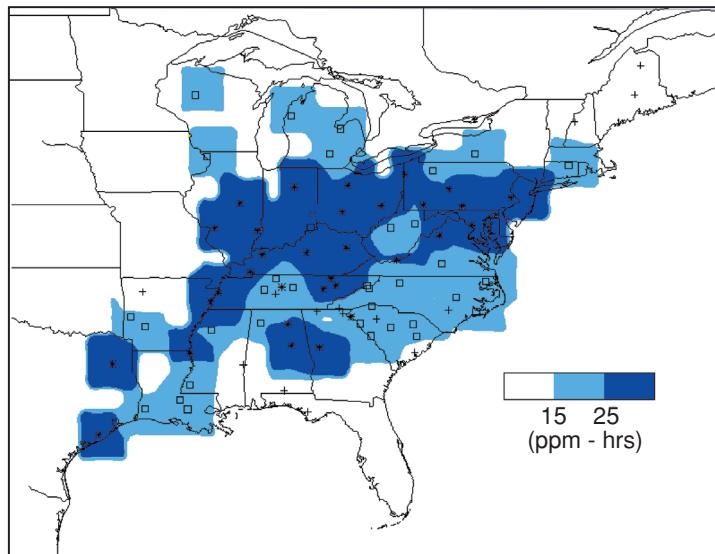
Despite the historical emphasis on local emission controls and the implementation of several federal control programs, observations in rural areas of North America show O<sub>3</sub> pollution to be ubiquitous to much of the North American continent. Observations in the 1970s indicated that photochemical smog can be regional in its spatial extent (i.e., 1000s of kilometers) and, given appropriate meteorological and topographic conditions, it can produce elevated concentrations of ground-level O<sub>3</sub> over rural as well as metropolitan areas (e.g., RTI, 1975; Decker, 1976; Wolff and Lioy, 1980). Data from recently established rural O<sub>3</sub> monitoring networks in the northeastern and southeastern United States, in California, and in portions of southern Canada have confirmed that rural O<sub>3</sub> pollution episodes do occur with 1-hr peak O<sub>3</sub> concentrations typically from 60 to 100 ppb (Saylor et al., 1998; Canadian - Vegetation, 1997). Figure 1.6 indicates the accumulated O<sub>3</sub> dosage over the eastern United States during the growing season of 1995. Analysis of these and similar rural O<sub>3</sub> observations in conjunction with empirically derived dose-response relationships between ambient O<sub>3</sub> and vegetation suggests that

these regional-scale episodes are severe enough, and recur often enough over a growing season, to have significant effects on the net productivity of agricultural crops, forests, and other ecosystems in portions of the North American continent (Heck and Cowling, 1997; Canadian - Vegetation, 1997).

The realization that O<sub>3</sub> pollution is regional in nature and can occur in rural as well as urban areas has sparked a reappraisal of policies and scientific understanding in North America. On the policy side this reappraisal has led to new initiatives to develop regional approaches to O<sub>3</sub> management (e.g., the Ozone Transport Assessment Group, discussed in Section 2.2.1). On the scientific and technical side, this reappraisal has led to a renewed effort to understand the mechanisms that cause long-range transport and urban-rural interchange. In turn, a reevaluation of the instrumentation, measurement strategies, and models used by the scientific community and their ability to characterize the processes that couple urban and rural pollution (see Section 3.6 and Chapter 4) is underway. This scientific reevaluation has provided a deeper understanding of the roles of VOC and NO<sub>x</sub> in fostering O<sub>3</sub> pollution and how these roles tend to evolve in time and space (see Chapter 3).

#### 1.1.4.2 *A Potentially Rising “Continental Background” Raises Additional Concerns*

There is now a growing body of evidence that suggests that the spread of O<sub>3</sub> pollution may extend beyond the regional scale to the continental, and even hemispheric scale. Detailed analyses of late 19<sup>th</sup> and early 20<sup>th</sup> century O<sub>3</sub> datasets indicate that free tropospheric O<sub>3</sub> in the northern hemisphere has undergone significant variations over the past century and continues to vary in some regions of the globe today. (e.g., Logan ,1988; Volz and Kley, 1988; Staehlein et al., 1994; Scheel et al. 1997). The evidence for long-term variations in free tropospheric O<sub>3</sub> is strongest in Europe where measurements of O<sub>3</sub> date back to the 1800s. For example, Volz and Kley (1988) used current techniques for measuring O<sub>3</sub> to recalibrate O<sub>3</sub> measurements made in Paris in the late 19<sup>th</sup> century. Their analysis indicates that surface O<sub>3</sub> concentrations at the end of the 1800s were about a



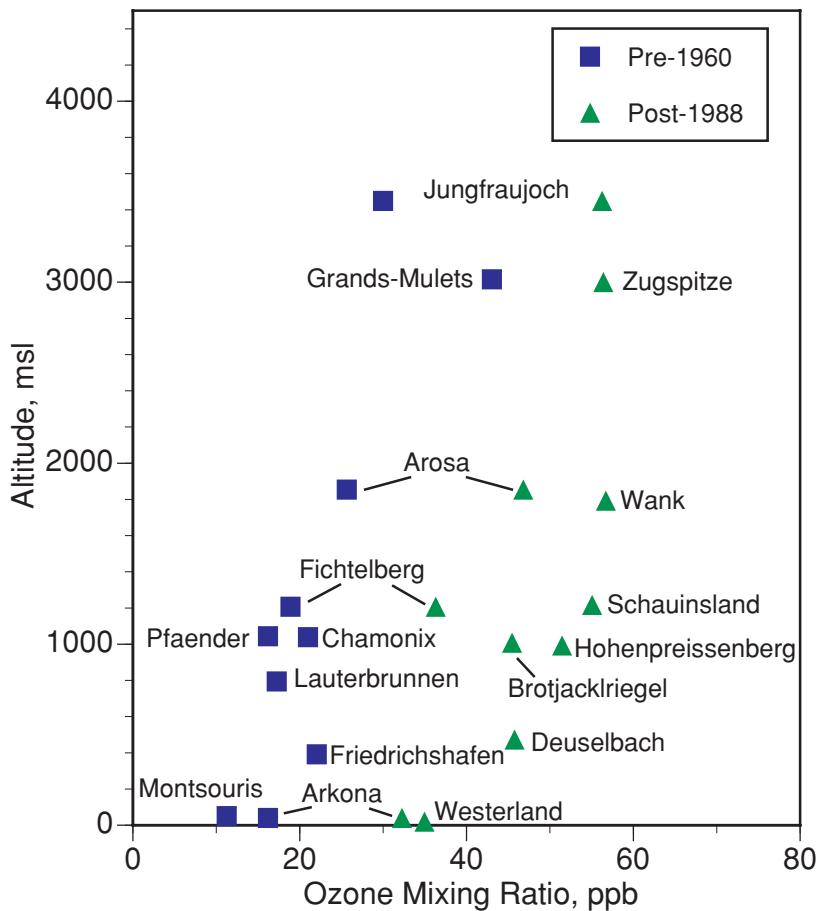
**Figure 1.6** Growing-season exposure of crops and other vegetation in the eastern United States to  $O_3$  in 1995 in terms of the crop-exposure indice “SUM06” (in ppm-hrs). The larger the SUM06 value the greater the potential damage to vegetation and the greater the probability crop yields will be depressed. Data from the U.S. National Crop Loss Assessment Network indicate that agricultural yields in North America are depressed, on average, by about 10% when SUM06-values exceed 15-25 ppm-hrs (Heck and Cowling, 1997, Canadian - Vegetation, 1997). SUM06 values shown here were calculated from an analysis of 85 rural  $O_3$  monitoring sites that comprise the SOS, SON, and EPA CASTNet networks. Locations of sites are indicated by: “+” for sites with  $SUM06 < 15$  ppm-hrs, “box” for sites with  $15 < SUM06 < 25$  ppm-hrs, and “\*\*” for sites with  $SUM06 > 25$  ppm-hrs. (After Saylor et al., 1998.)

factor of 2 less than current concentrations over Europe. More detailed analyses following Volz and Kley’s seminal paper have reached similar conclusions (see, for example, Figure 1.7).

Because there are no records of systematic  $O_3$  concentration measurements over North America before the mid-20<sup>th</sup> century, it is not possible to determine if a similar increase in  $O_3$  over North America has occurred. Nevertheless, the similarities between Europe and North America in terms of land use and land cover, pollutant emissions, and meteorology suggest that long-term trends in  $O_3$  over North America may be like those inferred for Europe. The implications of such a long-term  $O_3$  trend for understanding  $O_3$  pollution effects on humans and ecosystems and for possible future approaches to mitigate these effects have yet to be fully explored but could be considerable (see for example, Sections 3.1 and 3.8.)

## 1.2 REPORT STRUCTURE AND PRESENTATION – *What’s Here*

The audience for this assessment reflects a broad spectrum of policy-relevant and technical expertise. In view of this spectrum, the presentation is structured in a manner that addresses the needs of both disciplines. Chapter 2 provides an overview of the  $O_3$  management approaches that have been adopted by Canada, Mexico, and the United States. Chapter 3 summarizes key findings in the science of  $O_3$  pollution with specific emphasis on their relevance to the policy-making community. Chapter 4 focuses on Air-Quality Modeling Systems: their characteristics, recent improvements, and inherent limitations. Chapter 5 describes how the tools of the scientific community can be integrated into an  $O_3$  management scheme that is robust from a scientific point of view and accountable and responsive from a policy point of view. Chapter 6 concludes the assessment with a brief summary of major conclusions and recommendations for future directions.



**Figure 1.7** Surface O<sub>3</sub> concentrations of August/September from different locations in Europe as a function of altitude. Squares indicate averaged O<sub>3</sub> concentrations measured between 1896 (Grand Mulets) and 1940 (Pfander) and the triangles indicate averaged O<sub>3</sub> concentrations measured between 1988 and 1991. (After Staehlein et al., 1994.)

Throughout the document, textboxes are used to highlight information. These boxes contain informational or technical material and are marked accordingly:



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indicates technical details for the interested reader (green background).